Free Electron Gas (Quantum Treatment)

- Below the Fermi temperature, we can consider the state as a small deviation from the Fermi sea.
- As we'll see later, the properties of the free electron gas (= a set of electrons without mutual interaction in a uniform potential.) can be a good starting point for considering the properties of many materials.
- Here we summarize the basic properties of the free electron gas.
- Specific heat

The density of states at the Fermi level

$$C = \gamma T \qquad \gamma = \frac{2\pi^2}{3} k_B^2 \rho_F$$

- Spin susceptibility (Pauli's paramagnetism)

$$\chi_P = \mu_B^2 \rho_F$$

- Orbit susceptibility (Landau's diamagnetism)

$$\chi_L = -\frac{1}{3}\mu_B^2 \rho_F \quad \left(= -\frac{1}{3}\chi_P\right)$$

Specific Heat

- Target: $N = \sum_{k,\sigma} f_k$ and $E = \sum_{k,\sigma} f_k \epsilon_k$

where f_k is the fermi distribution $f_k \equiv \frac{1}{e^{\beta(\epsilon-\mu)}+1}$

and $\epsilon_k \equiv \frac{\hbar^2 k^2}{2m}$, $k = \frac{1}{\hbar}\sqrt{2m\epsilon}$

The wave number takes discrete values $k = \frac{2\pi}{L} \times (\text{integer})$

- Then the k-summation is replaced by the integral:

$$\sum_{k,\sigma} \cdots = 2\int \frac{d^3k}{\left(\frac{2\pi}{L}\right)^3} \cdots = \frac{L^3}{4\pi^3}\int d^3k \cdots = \frac{L^3}{4\pi^3}\int dk\, 4\pi k^2 \cdots = \frac{L^3}{\pi^2}\int d\epsilon \frac{\sqrt{2m}}{2\hbar}\frac{1}{\sqrt{\epsilon}}\frac{2m\epsilon}{\hbar^2}$$
$$= \frac{L^3 (2m)^{3/2}}{2\pi^2\hbar^3}\int d\epsilon \sqrt{\epsilon} \cdots$$

which yields the following form w.r.t. the density of states (DOE), $\rho(\epsilon)$,

$$\sum_{k,\sigma} \cdots \Rightarrow \Omega \int d\epsilon\, \rho(\epsilon) \cdots \qquad \rho(\epsilon) \equiv \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\sqrt{\epsilon}$$
$$\Omega \equiv L^3$$

Then our target is

$$N = \int d\epsilon\, \rho(\epsilon) f(\epsilon) \quad \text{and} \quad E = \int d\epsilon\, \rho(\epsilon)\cdot\epsilon\cdot f(\epsilon)$$

- Now, for an arbitrary function, $g(\epsilon)$, we consider

$$G \equiv \int d\epsilon\, f(\epsilon)\, g(\epsilon).$$

To focus on the small deviation from $T=0$, we decompose

$$f(\epsilon) = \theta(\mu-\epsilon) + \mathrm{sgn}(\epsilon-\mu) \times \frac{1}{e^{\beta|\epsilon-\mu|}+1}$$

The second term is odd w.r.t. $\epsilon-\mu \to -(\epsilon-\mu)$.

∘ By expanding $g(\epsilon) = \sum_{p=0}^{\infty} a_p (\epsilon-\mu)^p$,

$$G = \int d\epsilon\, f(\epsilon)\, g(\epsilon)$$

$$= \underbrace{\int^{\mu} d\epsilon\, g(\epsilon)}_{\substack{\parallel\\ G_0}} + \int_{-\infty}^{\infty} d(\epsilon-\mu)\ \mathrm{sgn}(\epsilon-\mu)\ \frac{\sum_{p} a_p (\epsilon-\mu)^p}{e^{\beta|\epsilon-\mu|}+1}$$

$$= G_0 + 2\sum_{p=1,3,5,\cdots} a_p \int_0^{\infty} d(\epsilon-\mu)\ \frac{(\epsilon-\mu)^p}{e^{\beta|\epsilon-\mu|}+1}$$

$$= G_0 + 2\sum_{p=1,3,5,\cdots} a_p \lambda_p T^{p+1}$$

where λ_p is defined as

$$\lambda_p \equiv \int_0^{\infty} d\xi\ \frac{\xi^p}{e^{\xi}+1} = \int_0^{\infty} d\xi\ \xi^p e^{-\xi} \sum_{n=0}^{\infty} e^{-n\xi}$$

$$= \sum_{n=0}^{\infty} \int_0^{\infty} d\xi\ e^{-(n+1)\xi}\ \xi^p$$

$$= \sum_{n=0}^{\infty} \frac{1}{(n+1)^{p+1}} \int_0^{\infty} d\tau\ e^{-\tau}\ \tau^p$$

$$= \Gamma(p+1)\ \zeta(p+1)$$

$$\lambda_1 = \Gamma(2)\cdot\zeta(2) = 1\cdot\frac{\pi^2}{6} = \frac{\pi^2}{6}$$

$$\lambda_3 = \Gamma(4)\cdot\zeta(4) = 6\cdot\frac{\pi^4}{90} = \frac{\pi^4}{15}$$

$$\therefore\ G \fallingdotseq G_0 + \frac{\pi^2}{3} g'(\mu) T^2 + \frac{2\pi^4}{15}\cdot 6\, g'''(\mu) T^4$$

$$= G_0 + \frac{\pi^2}{3} g'(\mu) T^2 + \frac{4\pi^4}{5} g'''(\mu) T^4$$

∘ Then for N $(g(\epsilon) = \rho(\epsilon))$

$$N/\Omega = \int_0^{\mu} d\epsilon\, \rho(\epsilon) + \frac{\pi^2}{3} \rho'(\mu) T^2 \quad \text{—①}$$

Since $N/\Omega = N(T=0)/\Omega = \int_0^{\epsilon_F} d\epsilon\, \rho(\epsilon)$,

$$① \rightarrow \quad N/\Omega = N/\Omega + (\mu - \epsilon_F)\rho(\mu) + \frac{\pi^2}{3}\rho'(\mu) T^2$$

$$\rightarrow \quad \mu - \epsilon_F = -\frac{\pi^2}{3}\frac{\rho'(\mu)}{\rho(\mu)} T^2 \doteqdot -\frac{\pi^2}{3}\frac{\rho_F'}{\rho_F} T^2$$

$$(\rho_F \equiv \rho(\epsilon_F) \quad \rho_F' \equiv \rho'(\epsilon_F))$$

For E $(g(\epsilon) = \rho(\epsilon)\cdot\epsilon)$

$$E/\Omega \doteqdot \int_0^{\mu} d\epsilon\, \rho(\epsilon)\epsilon + \frac{\pi^2}{3}(\rho\epsilon)' T^2$$

$$\doteqdot E_0/\Omega + (\mu - \epsilon_F)\rho_F \epsilon_F + \frac{\pi^2}{3}(\rho'\epsilon + \rho) T^2$$

$$\doteqdot E_0/\Omega - \frac{\pi^2}{3}\rho_F' \epsilon_F T^2 + \frac{\pi^2}{3}(\rho_F'\epsilon_F + \rho_F) T^2$$

$$= E_0/\Omega + \frac{\pi^2}{3}\rho_F T^2 \quad (\leftarrow \text{This } T \text{ means } k_B T)$$

$$\rightarrow \quad C/k_B = \frac{2\pi^2}{3}\rho_F k_B T \ (\text{per volume}) \quad \text{—①}$$

※ Note that we've not used any specific form of $\rho(\epsilon)$ in deriving ①. So, this equation should be valid any system described by the Fermi sea. For this reason, this equation is used for many normal metals.

Spin Susceptibility

- An electron in electro-magnetic field:

$$\mathcal{H} = \frac{1}{2m}\sum_i \left(\mathbf{p}_i + e\mathbf{A}(\mathbf{r}_i)\right)^2 + g\mu_B \mathbf{H}\cdot\sum_i \mathbf{s}_i$$

- First, we only consider the contribution from the Zeemann term. (i.e. we set $\mathbf{A}=0$)

$$\hat{\mathcal{H}} = \frac{\hbar^2}{2m}\sum_{\mathbf{k}\sigma} k^2 c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \frac{g}{2}\mu_B H \sum_{\mathbf{k}\sigma} \sigma c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}$$

$$= \sum_{\mathbf{k}\sigma}\left(\epsilon_{\mathbf{k}} + \frac{g}{2}\mu_B H\sigma\right) c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}$$

$$(\sigma = \pm 1)$$

$$M = -\sum_{\mathbf{k}\sigma}\left(\frac{g}{2}\mu_B\sigma\right)\langle c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}\rangle$$

$$= -\sum_{\mathbf{k}} \frac{g\mu_B}{2}\left\{ f\left(\epsilon_k + \frac{g\mu_B}{2}H\right) - f\left(\epsilon_k - \frac{g\mu_B}{2}H\right)\right\}$$

$$\underset{T\to 0}{=} \Omega\int d\epsilon\, \frac{\rho(\epsilon)}{2}\frac{g\mu_B}{2}\left\{\theta\left(\epsilon_F - \epsilon + \frac{g\mu_B H}{2}\right) - \theta\left(\epsilon_F - \epsilon - \frac{g\mu_B H}{2}\right)\right\}$$

$$\approx \Omega\rho_F \frac{g\mu_B}{4}(g\mu_B H)$$

$$m \equiv M/V \sim \frac{g^2\mu_B^2}{4}\rho_F H$$

$$\longrightarrow \quad \chi_P \sim \mu_B^2 \rho_F \quad (\because g \fallingdotseq 2) \qquad \text{—— (2)}$$

$$\mu_B = \frac{e\hbar}{2m} \quad \text{(Bohr magneton)}$$

(SI unit)

※ Eq. (2) is also derived with no reference to specific form of $\rho(\epsilon)$.

Landau's Diamagnetism

- Let us consider the Hamiltonian (of a single particle)

$$\mathcal{H} = \frac{1}{2m}\left(\mathbb{P} + e\mathbb{A}\right)^2 \qquad (q = -e)$$

$$\mathbb{B} = \begin{pmatrix} 0 \\ 0 \\ B \end{pmatrix} = \nabla \times \mathbb{A} \qquad B = \partial_x A_y - \partial_y A_x$$

$$\longrightarrow \mathbb{A} = \begin{pmatrix} 0 \\ Bx \\ 0 \end{pmatrix} \quad (\text{Landau gauge})$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\left(\partial_x^2 + \left(\partial_y + \frac{ie}{\hbar}Bx\right)^2 + \partial_z^2\right)$$

- Schrödinger equation

$$\mathcal{H}\psi = \epsilon\psi$$

Let's assume $\psi = e^{ik_y y + ik_z z}\, u(x)$. Then,

$$-\frac{\hbar^2}{2m}\left(\partial_x^2 + \left(ik_y + \frac{ieB}{\hbar}x\right)^2 - k_z^2\right)u = \epsilon u$$

$$-\frac{\hbar^2}{2m}\left(\partial_x^2 - \left(k_y + \frac{eB}{\hbar}x\right)^2 - k_z^2\right)u = \epsilon u$$

$$\left(\frac{1}{2m}p_x^2 + \frac{1}{2}\frac{e^2B^2}{m}\left(x + \frac{\hbar k_y}{eB}\right)^2\right)u = \left(\epsilon - \frac{\hbar^2 k_z^2}{2m}\right)u$$

This is the Schrödinger eq. of the harmonic oscillator with the oscillation frequency

$$\omega_0 = \frac{eB}{m} \quad (\text{cyclotron frequency})$$

and the center of oscillation $x_0 = -\dfrac{\hbar k_y}{eB}$.

Therefore, the eigenstates are specified by the 3 parameters, (n, k_y, k_z), and the corresponding eigen-energy is

$$\epsilon_{n k_y k_z} \equiv \hbar\omega_0\left(n+\frac{1}{2}\right) + \frac{\hbar^2 k_z^2}{2m}$$

which is degenerated with respect to k_y. (Landau level)

- Degeneracy of each Landau level.

Assuming the periodic boundary condition,
$k_y = -\frac{2\pi}{L_y} l_y$ with $l_y = 0, \pm1, \pm2, \cdots$

For each l_y, the center of the oscillation is

$$x_{l_y} \equiv \frac{\hbar}{eB}\frac{2\pi}{L_y} l_y$$

Because $x_{l_y} \in [0, L_x)$,

$$0 \leq \frac{h}{eBL_y} l_y < L_x \qquad 0 \leq l_y < \frac{eBL_xL_y}{h}$$

Therefore, for each Landau level, we have

$$\frac{2eBA}{h} = \frac{2m\omega_0}{h} A \qquad (A = L_xL_y)$$

degenerated states. ("2" comes from the spin degree of freedom)

- Free Energy.

We want to compute the contribution to the susceptibility from the deformation of the orbits of electrons. We can do that through the free energy.

$$G = -k_B T \log \Xi$$

$$\Xi = \prod_{\alpha} \left(1 + e^{-\beta(\epsilon_\alpha - \mu)}\right) \quad (\alpha = (n, l_y, l_z, \sigma))$$

- $$G = -k_B T \int_{\epsilon_0} d\epsilon\, \rho(\epsilon) \log\left(1 + e^{-\beta(\epsilon - \mu)}\right)$$

Introducing the integrated density of states

$$\varphi(\epsilon) \equiv \int_{\epsilon_0}^{\epsilon} d\epsilon'\, \rho(\epsilon') = \sum_{\alpha} \theta(\epsilon - \epsilon_\alpha)$$

$$G = -k_B T \int_{\epsilon_0}^{\infty} d\epsilon\, \varphi'(\epsilon) \log\left(1 + e^{-\beta(\epsilon - \mu)}\right)$$

$$= -k_B T \left[\varphi(\epsilon) \log\left(1 + e^{-\beta(\epsilon - \mu)}\right)\right]_{\epsilon_0}^{\infty}$$

$$-k_B T \int_{\epsilon_0}^{\infty} d\epsilon\, \varphi(\epsilon) \frac{\beta}{e^{\beta(\epsilon - \mu)} + 1}$$

$$\underset{T \ll T_F}{\simeq} -\Phi(\mu)$$

$$\Phi(\mu) \equiv \int_{\epsilon_0}^{\mu} d\epsilon\, \varphi(\epsilon) \doteqdot \Omega \times C \mu^{\frac{5}{2}} \left(1 - \frac{5}{32}\left(\frac{\hbar\omega_0}{\mu}\right)^2\right)$$

$$C \equiv \frac{4}{15} \rho_F \frac{1}{\sqrt{\epsilon_F}}$$ —— ※ $(m\omega_0 = eB)$

※1 Calculation of $\Phi(\mu)$

$$\Phi(\mu) = \int^{\mu} d\epsilon \; \varphi(\epsilon)$$

$$= \int^{\mu} d\epsilon \sum_{\alpha} \theta(\epsilon - \epsilon_\alpha) \qquad \alpha = (n, l_y, l_z)$$

$$= \int^{\mu} d\epsilon \, \frac{2m\omega_0}{h} A \sum_{n, l_z} \theta(\epsilon - \epsilon_n - \epsilon_z)$$

$$\left(\begin{array}{ll} \omega_0 = \dfrac{eB}{m} & \epsilon_n = \hbar\omega_0 \left(n + \frac{1}{2}\right) \\ \epsilon_z = \dfrac{\hbar^2}{2m}\left(\dfrac{2\pi l_z}{L_z}\right)^2 & A \equiv L_x L_y \end{array} \right)$$

$$\sum_{l_z = 0, \pm 1, \pm 2, \cdots} \theta(\epsilon - \epsilon_n - \epsilon_z) = 2 \times l_z^{max} \qquad \mathcal{O}(1) \to +\delta$$

$$\frac{\hbar^2}{2m}\left(\frac{2\pi l_z^{max}}{L_z}\right)^2 = \epsilon - \epsilon_n \qquad l_z^{max} = \frac{L_z}{2\pi}\sqrt{\frac{2m(\epsilon - \epsilon_n)}{\hbar^2}}$$

$$\therefore \; \Phi(\mu) = \frac{2m\omega_0}{h} A \frac{2\sqrt{2m}}{h} L_z \int_0^{\mu} d\epsilon \sum_n \left(\sqrt{\epsilon - \epsilon_n} + \mathcal{O}\left(\frac{1}{L_z}\right) \right)$$

$$= \frac{(2m)^{3/2}\omega_0 \Omega}{h^2} \frac{4}{3} \sum_n (\mu - \epsilon_n)^{3/2} + \cancel{\mathcal{O}(A)}$$

$$= \Omega \cdot \frac{4}{3} \frac{(2m)^{3/2}\omega_0}{h^2} \sum_n \left(\mu - \hbar\omega_0\left(n + \frac{1}{2}\right)\right)^{3/2}$$

$$= \Omega \cdot \frac{4}{3} \frac{(2m)^{3/2}\omega_0}{h^2} (\hbar\omega_0)^{3/2} \sum_{n=0}^{n_0 - 1} \left(n + \frac{1}{2}\right)^{3/2} \qquad \left(n_0 \equiv \frac{\mu}{\hbar\omega_0}\right)$$

$$= \Omega \cdot \frac{4}{3} \frac{(2m)^{3/2}\omega_0}{h^2} (\hbar\omega_0)^{3/2} \left(\frac{2}{5} n_0^{\frac{5}{2}} - \frac{1}{16} n_0^{\frac{1}{2}} \right) \cdots\cdots \#$$

$$= \Omega \cdot \frac{2(2m)^{3/2}}{15\pi^2\hbar^3} \mu^{\frac{5}{2}} \left(1 - \frac{5}{32}\left(\frac{\hbar\omega_0}{\mu}\right)^2 \right)$$

$$= \Omega \cdot c \cdot \mu^{\frac{5}{2}} \left(1 - \frac{5}{32}\left(\frac{\hbar\omega_0}{\mu}\right)^2 \right)$$

$$c \equiv \frac{2(2m)^{3/2}}{15\pi^2\hbar^3} = \frac{4}{15} \rho_F / \sqrt{\epsilon_F} \quad (\text{see } 5\text{-}2)$$

... a formula

$$\sum_{n=0}^{n_0-1} f(n+\tfrac{1}{2}) = \int_0^{n_0} dx \left(f(x) - \frac{1}{24} f''(x) \right) + \Delta(n_0)$$

When $\int^{n_0} dx\, f''(x) = O(n_0^\alpha)$ $(\alpha > 0)$,
the Δ-term can be neglected compared to $\int dx f''$ as $n_0 \to \infty$.

[Proof] Easy to show, starting from

$$\int_n^{n+1} dx\, f(x) = \int_n^{n+1} dx \sum_{k=0}^{\infty} \frac{1}{k!} f^{(k)}(n+\tfrac{1}{2}) \left(x - (n+\tfrac{1}{2})\right)^k$$

When $f(x) = x^{3/2}$, we have

$$\sum_{n=0}^{n_0-1} (n+\tfrac{1}{2})^{3/2} = \int_0^{n_0} dx\, x^{3/2} - \frac{1}{24} \left[\frac{3}{2} x^{1/2} \right]_0^{n_0}$$

$$= \frac{2}{5} \left[x^{\frac{5}{2}} \right]_0^{n_0} - \frac{1}{16} n_0^{1/2}$$

$$= \frac{2}{5} n_0^{\frac{5}{2}} - \frac{1}{16} n_0^{\frac{1}{2}} + o(n_0^{1/2})$$

◦ Magnetization

$$\mathcal{M} = -\frac{\partial G}{\partial B} = \frac{\partial \Phi}{\partial B}$$

$$= \Omega \times c\mu^{\frac{5}{2}} \left(-\frac{5}{16} \left(\frac{\hbar e}{m\mu} \right)^2 B \right)$$

$$\therefore \chi_L = -\frac{5}{16} c \left(\frac{\hbar e}{m} \right)^2 \sqrt{\mu}$$

$$\underset{\substack{\mu \to \epsilon_F \\ T \to 0}}{=} -\frac{5}{16} \frac{4}{15} \rho_F \left(\frac{\hbar e}{m} \right)^2$$

$$= -\frac{1}{3} \mu_B^2 \rho_F \qquad \left(\mu_B = \frac{e\hbar}{2m} \right)$$