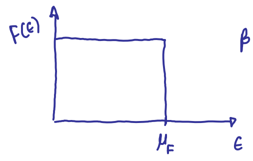
Free electron Fermi gas :

For Fermions: $\langle n_j \rangle_{F.D} = \dfrac{1}{e^{\beta(\epsilon_j - \mu)} + 1} = F(\epsilon_j)$

At Low T

C_V = Lattice vibrations + Free electrons

αT^3 $\qquad$ βT



$\beta = \infty \ (T=0)$

$\mu\big|_{T=0} = \mu_F$ "Fermi Energy"

$= \epsilon_F$

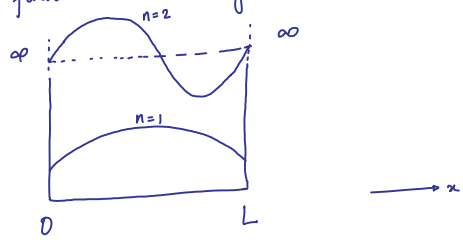
Total no. of Particles : $N = \sum_j \langle n_j \rangle$

Total Energy $E = \sum_j \epsilon_j \langle n_j \rangle$

} All temperatures

$\left.\begin{array}{l} N >> 1 \\ V >> 1 \end{array}\right\} n = N/V \rightsquigarrow$ finite $\quad$ "Thermodynamic limit"

Electron in a box :



$\psi(x) = \psi_0 \cdot \sin\left(\frac{n\pi x}{L}\right)$

$\vec{k} = (k_x, k_y, k_z)$

$= (n_x, n_y, n_z)\frac{\pi}{L}$

Exitations n_x, n_y, n_z are > 0

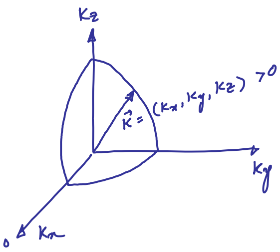
As the size $L \to \infty$, the k's become closed stacked.

$$\sum_{\vec{k}} \xrightarrow[\text{as } N,V \to \infty]{} \int \underbrace{g(k)}_{dN/dk} \, dk$$

To compute $g(k)$:

dN modes in some d^3k

$$= \frac{d^3k}{V_{min}} \cdot \underbrace{(2s+1)}_{s=1/2} \cdot \underbrace{\frac{1}{8}}_{n_{x,y,z} > 0}$$



dN modes in d^3k $= \dfrac{4\pi k^2\, dk}{(\pi/L)^3}\,(2s+1)\cdot\dfrac{1}{8}$

$$= \frac{(2s+1)\,V k^2\, dk}{2\pi^2} = g(k)\, dk$$

$$\Rightarrow \quad g(k) = \frac{(2s+1)\,V\,k^2}{2\pi^2} \qquad \text{--- } (1)$$

Lets compute $N = \int_{k=0}^{k=k_F} \underbrace{g(k)}_{dN/dk}\, dk$ At $T=0$

$$= \frac{(2s+1)}{2\pi^2}\cdot V\,\frac{k_F^3}{3}$$

$$k_F = \left(\frac{6\pi^2}{(2s+1)}\,\frac{N}{V}\right)^{1/3}$$

Compute Fermi energy: $\epsilon_F = \dfrac{\hbar^2 k_F^2}{2m} = \dfrac{\hbar^2}{2m}\left(\dfrac{6\pi^2}{(2s+1)}\,\dfrac{N}{V}\right)^{2/3}$

Compute Fermi temperature: $T_F \simeq \dfrac{\epsilon_F}{k_B} \simeq \dfrac{\hbar^2}{2mk_B}\left(\dfrac{6\pi^2}{2s+1}\cdot\dfrac{N}{V}\right)^{2/3}$

$$g(k)\,dk = \frac{(2s+1)\,Vk^2}{2\pi^2}\,dk = \rho(\epsilon)\,d\epsilon \qquad \text{--- } (2)$$

To get $\rho(\epsilon)$ "Density of states in terms of ϵ"

$$\rho(\epsilon) = dN/d\epsilon$$

$$\int_0^{k_F} g(k)\,dk = \int_0^{\epsilon_F} \rho(\epsilon)\,d\epsilon$$

$$g(k)\,dk = \frac{(2s+1)\,Vk^2}{2\pi^2}\,dk$$

Using the fact that $\epsilon = \dfrac{\hbar^2 k^2}{2m} \Rightarrow k^2 = \dfrac{2m\epsilon}{\hbar^2}$

$$dk = \frac{1}{k}\cdot\frac{m\,d\epsilon}{\hbar^2}$$

Take Cu for eg:

$n = \dfrac{N}{V} = 10^{28}/m^3$

$k_F \sim 10^9/m$

$\epsilon_F \sim 10^{-68}\cdot 10^{31}\cdot 10^{18}$ J $\sim 10^{-19}$ J $\sim$ eV

$T_F \sim 10^{-19}\, 10^{23}$ K $\sim 10^4$ K

At room temperature: $T = 300$ K

$$\frac{T}{T_F} \ll 1$$

Related to the fraction of excited electrons at T.

$$dk = \left(\frac{\hbar^2}{2m\epsilon}\right)^{1/2} \frac{m\, d\epsilon}{\hbar^2}$$

$$\therefore \quad g(k)\,dk = \frac{(2s+1)\,V}{2\pi^2} \cdot \left(\frac{2m\epsilon}{\hbar^2}\right)\left(\frac{\hbar^2}{2m\epsilon}\right)^{1/2} \frac{m}{\hbar^2}\, d\epsilon$$

$$= \underbrace{(2s+1)\frac{V m}{2\pi^2\hbar^2}\left(\frac{2m}{\hbar^2}\right)^{1/2} \epsilon^{1/2}}_{\rho(\epsilon)}\, d\epsilon$$

$$\rho(\epsilon) = \frac{(2s+1)\,V m}{2\pi^2\hbar^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\epsilon^{1/2} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2} \quad \text{--- (3)}$$

Recalling $\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{(2s+1)}\frac{N}{V}\right)^{2/3} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$

$$\therefore \left(\frac{2m}{\hbar^2}\right)^{3/2} = \frac{1}{\epsilon_F^{3/2}}\left(\frac{3\pi^2 N}{V}\right) \quad \text{--- (4)}$$

Substituting (4) in (3), gives —

$$\rho(\epsilon) = \frac{\cancel{V}}{2\cancel{\pi^2}} \cdot \frac{1}{\epsilon_F^{3/2}}\left(\frac{3\cancel{\pi^2} N}{\cancel{V}}\right)\epsilon^{1/2}$$

$$\boxed{\rho(\epsilon) = \frac{3}{2}\frac{N}{\epsilon_F^{3/2}}\,\epsilon^{1/2}} \quad \text{--- (5)}$$

At $T=0$: $\int_0^{\epsilon_F} \rho(\epsilon)\,d\epsilon = \cancel{\frac{3}{2}} \frac{N}{\cancel{\epsilon_F^{3/2}}} \cdot \cancel{\epsilon_F^{3/2}} \cdot \cancel{\frac{2}{3}} = N$

In the thermodynamic limit & $T \neq 0$:

$$N = \int_{\epsilon=0}^{\infty} \rho(\epsilon)\,F(\epsilon)\,d\epsilon \quad \text{--- (6)}$$

$$E = \int_{\epsilon=0}^{\infty} \rho(\epsilon)\,\epsilon\,F(\epsilon)\,d\epsilon \quad \text{--- (7)}$$

$N = \sum_j \langle n_j \rangle = \sum_j F(\epsilon_j)$

$\sum_j \rightarrow \int \rho(\epsilon)\,d\epsilon.$

$\sum_j F(\epsilon_j) \longrightarrow \int_0^{\epsilon_F} \rho(\epsilon)\,\underset{T=0}{F(\epsilon)}\,d\epsilon$

$\longrightarrow \int_0^{\infty} \rho(\epsilon)\,\underset{T\neq 0}{F(\epsilon)}\,d\epsilon$

Both (6) & (7) are of type:

$$I = \int_0^\infty \phi(\epsilon)\, F(\epsilon)\, d\epsilon \quad \ldots \text{ in (6)}: \phi(\epsilon) = g(\epsilon)$$
$$\ldots \text{ in (7)}: \phi(\epsilon) = \epsilon\, g(\epsilon)$$

$\phi(\epsilon)$ is a function that is smooth

$$\phi(\epsilon) = \frac{d\psi(\epsilon)}{d\epsilon}$$

$$\boxed{\psi(\epsilon) = \int_0^\epsilon \phi(\epsilon')\, d\epsilon'}$$

" Fundamental theorem of calculus "

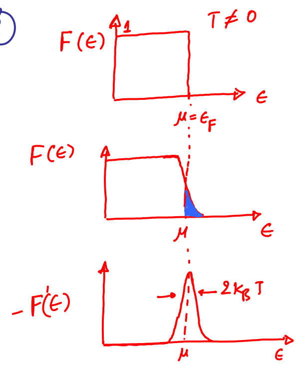
Computing I:

$$\int_0^\infty F(\epsilon)\, \phi(\epsilon)\, d\epsilon = \cancel{F(\epsilon)\,\psi(\epsilon)\Big|_0^\infty} - \int_0^\infty F'(\epsilon)\,\psi(\epsilon)\, d\epsilon \quad \ldots\ldots \because \int \phi(\epsilon')d\epsilon' = \psi(\epsilon')$$

$F(\infty) = 0$

$\psi(0) = 0$

$$\int_0^\infty F(\epsilon)\,\phi(\epsilon)\, d\epsilon = -\int_0^\infty F'(\epsilon)\,\psi(\epsilon)\, d\epsilon \qquad (8)$$



$\psi(\epsilon)$ is smooth around $\epsilon = \mu$,

Expand $\psi(\epsilon)$ in powers of $(\epsilon - \mu)$

$$\psi(\epsilon) = \sum_{m=0}^{\infty} \frac{1}{m!} (\epsilon - \mu)^m \frac{\partial^m \psi}{\partial \epsilon^m}\Big|_{\epsilon=\mu} \qquad (9)$$

Plugging (9) in (8), gives —

$$\int_0^\infty F(\epsilon)\,\phi(\epsilon)\, d\epsilon = -\int_0^\infty F'(\epsilon) \sum_{m=0}^{\infty} \frac{1}{m!} (\epsilon-\mu)^m \frac{d^m}{d\epsilon^m}\psi(\epsilon)\Big|_{\epsilon=\mu} d\epsilon$$

$$= -\sum_{m=0}^{\infty} \frac{1}{m!} \frac{d^m \psi(\epsilon)}{d\epsilon^m}\Big|_{\epsilon=\mu} \int_0^\infty F'(\epsilon)\,(\epsilon-\mu)^m\, d\epsilon$$

ϵ = Energy

μ = Chemical potential

$T = 0$, $\mu \to \epsilon_F$

Substituting for $F(\epsilon) = \dfrac{1}{e^{\beta(\epsilon-\mu)}+1}$

$$F'(\epsilon) = \frac{-e^{\beta(\epsilon-\mu)}\beta}{\left(e^{\beta(\epsilon-\mu)}+1\right)^2}$$

Plugging this in previous eqn:

$$\int_0^\infty F(\epsilon)\,\phi(\epsilon)\,d\epsilon = \sum_{m=0}^{\infty} \frac{1}{m!}\frac{d^m}{d\epsilon^m}\psi(\epsilon)\Big|_{\epsilon=\mu} \int_0^\infty \frac{\beta e^{\beta(\epsilon-\mu)}}{\left(e^{\beta(\epsilon-\mu)}+1\right)^2}(\epsilon-\mu)^m\,d\epsilon$$

Substituting for $(\epsilon-\mu)\beta = x$

$\beta\,d\epsilon = dx$

$$\int_0^\infty F(\epsilon)\,\phi(\epsilon)\,d\epsilon = \sum_{m=0}^{\infty} \frac{\beta^{-m}}{m!}\frac{d^m}{d\epsilon^m}\psi(\epsilon)\Big|_{\epsilon=\mu} \int_{-\beta\mu}^{\infty} \frac{e^x x^m}{(e^x+1)^2}\,dx \quad \text{—— (10)}$$

At low temp $-\beta\mu \longrightarrow -\infty$

$T \to 0,\ \beta \to \infty$

$$\int_0^\infty F(\epsilon)\,\phi(\epsilon)\,d\epsilon = \sum_{m=0}^{\infty} \frac{\beta^{-m}}{m!}\frac{d^m}{d\epsilon^m}\psi(\epsilon)\Big|_{\epsilon=\mu} \int_{-\infty}^{+\infty} \frac{e^x x^m}{(e^x+1)^2}\,dx \quad \text{—— (11)}$$

The integral $\displaystyle\int_{-\infty}^{\infty} \frac{e^x x^m}{(e^x+1)^2}\,dx = 0$, if m is odd

$$\int_{-\infty}^{+\infty} \frac{x^m}{(e^x+1)(e^{-x}+1)}\,dx$$

exists only for $m = 0, 2, 4, \ldots$

For $m = 0$: $\displaystyle\int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2}\,dx = \int_{t=1}^{\infty} \frac{dt}{t^2}$ ..... $e^x + 1 = t$

$$= \left.\frac{-1}{t}\right|_1^{\infty} = 1$$

For $m = 2$: $\displaystyle\int_{-\infty}^{+\infty} \frac{e^x \cdot x^2}{(e^x+1)^2}\,dx = \frac{\pi^2}{3}$ ..... Follow up the Math. Prequisites!

Plugging for $m = 0, 2$ in eq^n (1)

$$\int_{\epsilon=0}^{\infty} F(\epsilon)\,\phi(\epsilon)\,d\epsilon = \Psi(\epsilon)\Big|_{\epsilon=\mu} + \frac{(k_B T)^2}{2!}\cdot\frac{\pi^2}{3}\cdot\frac{d^2}{d\epsilon^2}\Psi(\epsilon)\Big|_{\epsilon=\mu} + \cancelto{0}{O\left[(k_B T)^4\right]}$$

$$\int_{\epsilon=0}^{\infty} F(\epsilon)\,\phi(\epsilon)\,d\epsilon = \int_{\epsilon=0}^{\mu} \phi(\epsilon)\,d\epsilon + (k_B T)^2\,\frac{\pi^2}{6}\,\frac{d\phi(\epsilon)}{d\epsilon}\Big|_{\epsilon=\mu} \quad \text{———} \quad (12)$$

$\because\ \Psi = \int \phi(\epsilon)\,d\epsilon$

... To compute N & E .....

For N: $\phi(\epsilon) = g(\epsilon)$

$$N = \int_{\epsilon=0}^{\infty} F(\epsilon)\,g(\epsilon)\,d\epsilon = \int_{\epsilon=0}^{\mu} g(\epsilon)\,d\epsilon + (k_B T)^2\,\frac{\pi^2}{6}\,\frac{d\,g(\epsilon)}{d\epsilon}\Big|_{\epsilon=\mu}$$

Now $g(\epsilon) = \frac{3}{2}\frac{N}{\epsilon_F^{3/2}}\,\epsilon^{1/2}$

$$\cancel{N} = \frac{\cancel{3}}{\cancel{2}}\frac{\cancel{N}}{\epsilon_F^{3/2}}\cdot \mu^{3/2}\cdot\frac{\cancel{2}}{\cancel{3}} + (k_B T)^2\,\frac{\pi^2}{6}\cdot\frac{3}{2}\cdot\frac{\cancel{N}}{\epsilon_F^{3/2}}\,\frac{1}{2}\,\mu^{-1/2}$$

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

Use this to derive $\mu(T)$!

$$\epsilon_F^{3/2} = \mu^{3/2}\left[1 + (K_B T)^2 \frac{\pi^2}{8} \mu^{-2}\right]$$

$$\epsilon_F = \mu\left[1 + (K_B T)^2 \frac{\pi^2}{8} \mu^{-2}\right]^{2/3}$$

$$\mu = \epsilon_F\left[1 + \frac{\pi^2}{8}\cdot\left(\frac{K_B T}{\mu}\right)^2\right]^{-2/3}$$

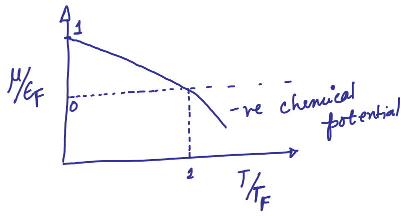
For low T: $K_B T/\mu << 1$

$$\underbrace{\mu = \epsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{K_B T}{\mu}\right)^2\right]}_{\text{Requires } \mu\,!}$$

" How $\mu = \mu(T)$ "

At low T: $T \to 0$, $\mu \to \epsilon_F$

$$\mu = \epsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{K_B T}{\epsilon_F}\right)^2\right]$$



Total Energy: $E = \int_{\epsilon=0}^{\infty} \underline{\underline{g(\epsilon)}}\ \underline{\underline{\epsilon}}\ \underline{\underline{F(\epsilon)}}\, d\epsilon$ In thermodynamic limit

Thus Plugging $\phi(\epsilon) = g(\epsilon)\,\epsilon$ in eq^n (12)

$$E = \int_0^{\infty} \epsilon\, g(\epsilon)\, F(\epsilon)\, d\epsilon = \int_{\epsilon=0}^{\mu} \underbrace{g(\epsilon)\,\epsilon}_{\phi(\epsilon)}\, d\epsilon + \frac{\pi^2}{6}(K_B T)^2 \frac{d}{d\epsilon}\underbrace{(g(\epsilon)\epsilon)}_{\phi(\epsilon)}\Bigg|_{\epsilon=\mu}$$

Since, $g(\epsilon) = \frac{3}{2}\frac{N}{\epsilon_F^{3/2}}\,\epsilon^{1/2}$

$$E = \frac{3}{2}\frac{N}{\epsilon_F^{3/2}}\left[\epsilon^{5/2}\cdot\frac{2}{5}\Big|_0^{\mu} + \frac{\pi^2}{6}(K_B T)^2\,\frac{3}{2}\cdot\epsilon^{1/2}\Big|_{\epsilon=\mu}\right]$$

$$E = \frac{3}{2}\frac{N}{\epsilon_F^{3/2}}\left[\frac{2}{5}\mu^{5/2} + \frac{\pi^2}{4}(k_B T)^2 \mu^{1/2}\right]$$

$$E = \frac{3}{5} N \epsilon_F \left[\left(\frac{\mu}{\epsilon_F}\right)^{5/2} + \frac{5\pi^2}{8}\left(\frac{k_B T}{\epsilon_F}\right)^2 \left(\frac{\mu}{\epsilon_F}\right)^{1/2}\right]$$

.... can be simplified further.....

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

$$E = \frac{3}{5} N \epsilon_F \left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2 \cdot \frac{5}{2} + \frac{5\pi^2}{8}\left(\frac{k_B T}{\epsilon_F}\right)^2 \left(1 - \frac{\pi^2}{24}\left(\frac{k_B T}{\epsilon_F}\right)^2\right)\right]$$

..... $k_B T/\epsilon_F << 1$

$\therefore \left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2\right]^n = 1 - \frac{\pi^2 n}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2$

Dropping $\left(\frac{k_B T}{\epsilon_F}\right)^4$ ....

$$E = \frac{3}{5} N \epsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2\right]$$ —— Final result.

as $T \to 0$

$E \neq 0$ in fact: $E = \frac{3}{5} N \epsilon_F$ "Not thermal Energy"

At $T \neq 0$, $C_V = \frac{dE}{dT} = \frac{\cancel{3}}{\cancel{5}} N \cancel{\epsilon_F} \cdot \frac{\cancel{5}\pi^2}{\cancel{12}_{2}} \frac{k_B^2}{\epsilon_F^{\cancel{2}}} \cancel{2} T$

$$\approx \frac{\pi^2}{2} N \frac{k_B^2 T}{\epsilon_F}$$

$\epsilon_F \approx k_B T_F$

$$C_V \approx \frac{\pi^2}{2} \cdot N k_B \, T/T_F \approx \frac{\pi^2}{2} \cdot \left(N\left(\frac{T}{T_F}\right)\right) k_B$$

$$C_v \approx \frac{\pi^2}{2} N' k_B$$

$N' = N \frac{T}{T_F}$ = No. of $e^{\ominus}$'s that contribute to C_v.

$\longrightarrow N$ as $T \longrightarrow T_F \ (10^4 K)$

Fraction of $e^{\ominus}$'s that participate in conduction (& C_v) are $\frac{N'}{N} = \frac{T}{T_F}$

at Room temperature $\frac{N'}{N} \sim \frac{1}{10^2} \sim 1\%$

$$C_V^{\text{overall}} = \underbrace{\alpha T^3}_{\text{Lattice contribution "Bosons"}} + \underbrace{\beta T}_{\text{Free electrons "Fermion"}} \qquad \text{At low } T.$$

$$\approx 3 N K_B \qquad \text{At high } T$$