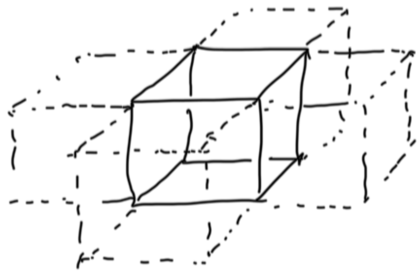
Sommerfeld theory of metals

Wavefn of free electron in a "box" open on all sides

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

The "box" "periodically" repeats to fill up the entire space $-\infty$ to $+\infty$



Finally we can make $L \to \infty$ to reach thermodynamic limit.

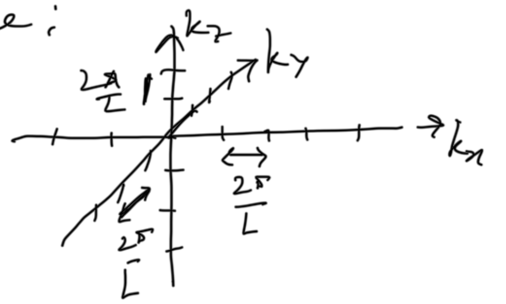
Periodicity of wavefn : Born - von - Karman periodic boundary condition (BVK PBC)

$$\left.\begin{aligned}\psi(x,y,z+L)&=\psi(x,y,z)\\ \psi(x,y+L,z)&=\psi(x,y,z)\\ \psi(x+L,y,z)&=\psi(x,y,z)\end{aligned}\right\}\quad e^{ik_xL}=e^{ik_yL}=e^{ik_zL}=1$$

$$\Rightarrow k_x=n_x\frac{2\pi}{L},\ k_y=n_y\frac{2\pi}{L},\ k_z=n_z\frac{2\pi}{L}$$

n_x, n_y, n_z integers.

$\Rightarrow$ k space:



$\Rightarrow$ volume of k space containing one state= $\left(\frac{2\pi}{L}\right)^3=\frac{8\pi^3}{V}$

Number of states contained in k space volume Ω : $\dfrac{\Omega}{\left(\frac{8\pi^3}{V}\right)}$

At $T=0$

To accommodate N electron we start filling up $\vec{k}$ states from $\vec{k}=0$ in 3D each with 2 electrons

If N is finite then we will fill up upto a certain magnitude of $\vec{k}$ say k_F

F→Fermi

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

$\Rightarrow \boxed{n=\frac{k_F^3}{3\pi^2}}$ $\quad p_F=\hbar k_F \rightarrow$ Fermi momentum $\propto n^{1/3}$

Fermi energy $E_F=\frac{\hbar^2k_F^2}{2m}=\frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}\propto n^{2/3}$

$$\text{Total energy } E=2\sum_{k<k_F}\frac{\hbar^2}{2m}k^2=2\frac{1}{\Delta k}\sum\frac{\hbar^2}{2m}k^2\Delta k$$
$$=2\left(\frac{V}{8\pi^3}\right)\int_0^{k_F}\frac{\hbar^2}{2m}k^2\,d^3k$$

$$\Rightarrow \frac{E}{V}=\frac{1}{4\pi^3}\int_0^{k_F}(4\pi k^2)\frac{\hbar^2k^2}{2m}dk=\frac{1}{\pi^2}\frac{\hbar^2k_F^5}{10m}\quad \text{at } \underline{T=0}$$

$$u=\frac{E}{N}=\frac{E/V}{N/V}=\frac{\frac{1}{\pi^2}\frac{\hbar^2k_F^5}{10m}}{\frac{k_F^3}{3\pi^2}}=\frac{3}{10}\frac{\hbar^2k_F^2}{m}=\underline{\frac{3}{5}E_F=\frac{3}{5}k_BT_F}\quad \text{at } \underline{T=0}$$

$\therefore$ Cl estimate: $\frac{3}{2}k_BT \rightarrow$ Q estimate: $\frac{3}{5}k_BT_F$ if $\rightarrow \frac{2}{5}T_F\approx 10^4K$
of $\frac{E}{N}$ $\qquad$ of E/N

Pressure exerted by electron gas:

$P=-\frac{\partial E}{\partial V}\Big|_N$ $\qquad$ Note $E=N\frac{3}{5}E$ $\qquad$ Recall $\frac{N}{V}=k_F^3/3\pi^2$

Recall, $dU=TdS-PdV$ $\qquad \frac{\partial E}{\partial V}=\frac{3N}{5}\frac{\partial E_F}{\partial V}=\frac{3}{5}\frac{\hbar^2}{2m}(3\pi^2)^{2/3}N^{2/3}\Big]\left(\frac{-2}{3}\right)V^{-5/3}$,

$\Rightarrow -\frac{\partial U}{\partial V}\Big|_S = P$

$S = k \ln \Omega$

Ω depends on N

$$= \frac{3}{5} N \left(-\frac{2}{3}\right) \frac{V}{V} [\quad] V^{-1/3}$$

$$= -\frac{2N}{5} \frac{1}{V} E_F = -\frac{2}{5} \frac{1}{V} N E_F = -\frac{2}{5} \frac{1}{V} \frac{5}{3} E = -\frac{2E}{3V}$$

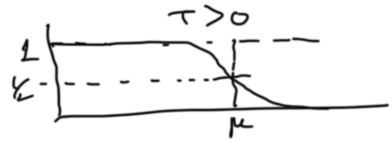
At $T=0$ $\Rightarrow \boxed{P = \frac{2}{3} \frac{E}{V}}$ $\Rightarrow$ Bulk modulus $= \frac{1}{\text{Compressibility } k} = -V \frac{\partial P}{\partial V} = \frac{2}{3} n E_F$

$\downarrow$

Mostly gives values incorrect order of magnitude

For $T > 0$

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



$\mu = E_F$ only at $T=0$

Although mostly valid till room temp.

$$U = 2 \sum_k E(k)\, f(E(k))$$

Like above $U = \frac{V}{4\pi^3} \int d\vec{k}\, E(\vec{k})\, f(E(\vec{k}))$ Similarly $N = \frac{V}{4\pi^3} \int d\vec{k}\, f(E(\vec{k}))$

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

$k = \sqrt{\frac{2mE}{\hbar^2}}$

$dk = \sqrt{\frac{2m}{\hbar^2}} \frac{E^{-1/2}}{2} dE$

$$= \frac{V}{4\pi^3} \int_0^\infty (4\pi k^2 dk)\, E(k)\, f(E(k))$$

$$= V \int_0^\infty \frac{1}{\pi^2} \frac{2mE}{\hbar^2} \sqrt{\frac{2m}{\hbar^2}} \frac{E^{-1/2}}{2} dE\, E\, f(E)$$

$$= V \int_0^\infty \left\{\frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2mE}{\hbar^2}}\right\} dE\, E\, f(E)$$

$$= V \int_0^\infty g(E)\, E(k)$$

$\rightarrow$ Do not feel other electrons.

$\therefore V\, g(E)\, dE \rightarrow$ number of "one electron" states in any range E to $E + dE$

$$g(E) = \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2mE}{\hbar^2}}$$

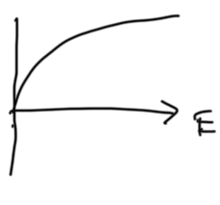
Recall at $T=0$: $n = \frac{k_F^3}{3\pi^2}$; $E_F = \frac{\hbar^2 k_F^2}{2m}$

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

$g(E)$

$$\therefore g(E) = \frac{1}{\pi^2} \frac{1}{2} \frac{(n\, 3\pi^2)^{2/3}}{E_F} \sqrt{\frac{(n\, 3\pi^2)^{2/3} E}{E_F}}$$

$$= \frac{(n\, 3\pi^2)}{2\pi^2} \frac{1}{E_F} \sqrt{\frac{E}{E_F}} \rightarrow g(E) \propto E^{1/2} \rightarrow$$



$$g(E) = \frac{3}{2} \frac{n}{E_F} \sqrt{\frac{E}{E_F}} \longrightarrow g(E) = \frac{3}{2} \frac{n}{E_F}$$

To calculate specific heat at $T \rightarrow 0^+$ we need to calculate dU with small change in T. above 0K.

for free electron gas with $n\left(=\frac{N}{V}\right)$

Recall, $T_F \approx 10^4\,K$ for $k_B T_F = E_F$ ... of typical metals (Na, K, Au, Ag ...)

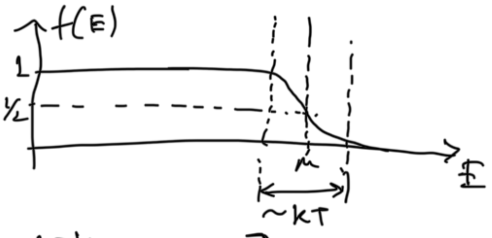
$k_B = 8.6 \times 10^{-5}\, eV/K \approx 10^{-4}\, eV \approx 10^{-5}\, Ha$, Ha: Hartree (atomic unit of energy) $= 27\,eV$

$\therefore k_B T_F \approx 1\, eV \sim 0.1\, Ha \sim E_F \sim u(T=0)$ Recall, $\underset{at\, T=0}{u} = \frac{3}{5} E_F$ for free independent electron gas

Room temperature : $k_B T \sim 10^{-2}\, eV \sim 10^{-3}\, Ha$

$\Rightarrow$ At room temp : $k_B T \sim 10^{-2} \times E_F$

Note the form of $f(E) = \dfrac{1}{e^{(E-\mu)/kT} + 1}$ $\Rightarrow$



f(E) falls from 1 to less than 0.01

for $E - \mu = 6kT \rightarrow 10^{-3}\, eV$ for 10 K $\longrightarrow$

$\longrightarrow 10^{-2}\, eV$ for 100

$\therefore$ At 10 K ~ 100 K : $\{E g(E)\}$ (~ 1 eV at) drops by less than 1% within the range of fall of $f(E)$ from 1 to less than 0.01

$\therefore$ To evaluate $\int_{-\infty}^{+\infty} \{E\, g(E)\} f(E)\, dE$ close to $T=0$, typically 10 K ~ 100 K,

we can expand $\{E\, g(E)\}$ about $E = \mu$ and keep only few terms in Taylor Eq^n.

For a general fn $\phi(E)$ Sommerfeld gave the expansion as :

$$\int_{-\infty}^{+\infty} \phi(E) f(E)\, dE = \int_{-\infty}^{\mu} \phi(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 \phi'(E)\Big|_{E=\mu} + \#(k_B T)^4 \phi'''(E)\Big|_{E=\mu} + \#(k_B T)^6 \ldots$$

for u : $\phi(E) = E\, g(E)$

n ; $\phi(E) = g(E)$

As $T \to 0^+$ (10 K ~ 100 K)

$$u = \int_0^{\mu} E\, g(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 \left[\mu g'(\mu) + g(\mu)\right]$$

$$n = \int_0^{\mu} g(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 g'(\mu)$$

setting the lower limit of $-\infty$ to 0 for free ...

$$= \underbrace{\int_0^{E_F} g(E)\,dE}_{n \text{ at } T=0} + \int_{E_F}^{\mu} g(E)\,dE + \frac{\pi^2}{6}(k_B T)^2 g'(\mu)$$

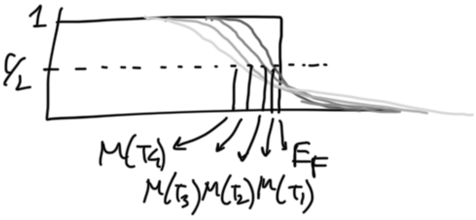
since lowest energy is zero.

Since $E_F \approx \mu$ → well within 0.01 of each other.

$$\therefore\ n \approx n + g(E_F)(\mu - E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F)$$

$$\Rightarrow 0 = g(E_F)(\mu - E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F)$$

$$\Rightarrow \boxed{\mu = E_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(E_F)}{g(E_F)}}$$



$T_4 > T_3 > T_2 > T_1 > 0$

Similarly:

$$U = \int_0^{E_F} E g(E)\,dE + \int_{E_F}^{\mu} E g(E)\,dE + \frac{\pi^2}{6}(kT)^2\left[\mu g'(\mu) + g(\mu)\right]$$

with approximation $\mu \approx E_F$

$$u = U_0 + E_F g(E_F)(\mu - E_F) + \frac{\pi^2}{6}(kT)^2 E_F g'(E_F) + \frac{\pi^2}{6}(kT)^2 g(E_F)$$

$$= U_0 + E_F\Big[\underbrace{g(E_F)(\mu - E_F) + \frac{\pi^2}{6}(k_B T)^2 g'(E_F)}_{0}\Big] + \frac{\pi^2}{6}(k_B T)^2 g(E_F)$$

$$= U_0 + \frac{\pi^2}{6}(kT)^2 g(E_F)$$

$$\Rightarrow C_V = \left.\frac{\partial U}{\partial T}\right|_{n \text{ (ie, fixed } V)} = \frac{\pi^2}{6} 2k^2 g(E_F)\, T = \frac{\pi^2}{6} 2k^2 \frac{m}{\pi^2 \hbar^2}\sqrt{\frac{2mE_F}{\hbar^2}}\, T$$

$$= \frac{mk^2}{3\hbar^2}\sqrt{\frac{2m}{\hbar^2}}\, E_F^{1/2}\, T \propto n^{1/3} T$$

$$\because E_F \propto n^{2/3}$$

No observable contribution at room temp.