Sommerfeld Theory of Metals

- So far we have ignored that we have a multi e^- system. (we solved a non interacting e^- problem)
- We will still continue with this (e^--e^- interactions will come soon!)

- Instead of moving forward, lets actually simplify even more $\Rightarrow$ ignore lattice! (i.e, forget about Bloch e^-)

$\Rightarrow$ Sommerfeld Model

* Metal with m conduction e^- per atom. ($N = m \cdot \#$ at)
* These e^- feel a constant potential througout the crystal

$$\left[\frac{\hbar^2}{2m}\nabla^2 + \underbrace{\epsilon_c}_{\text{no Fourier components except } V_0 = \epsilon_c}\right]\psi(r) = \epsilon\,\psi(r)$$

- $\psi_k = \frac{1}{\sqrt{V}} e^{ikr}$

$$\epsilon_k = \epsilon_c + \frac{\hbar^2 k^2}{2m}$$

We set to ϕ for simplicity

* We have N free e^- in Volume V. ($n = \frac{N}{V} \equiv$ density)

→ Useful parameter: r_s → radius of sphere containing $1e^-$

$$\text{Vol}/e^- = \underbrace{\frac{V}{N}}_{1/n} = \frac{4}{3}\pi r_s^3 \; ; \; r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$$

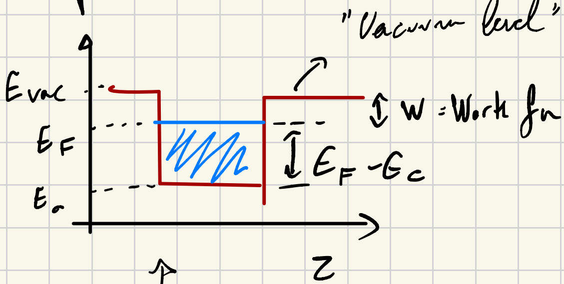
We usualy make it dimensionless

$$\rightarrow r_s' = \frac{r_s}{a_B}$$ → Bohr radius

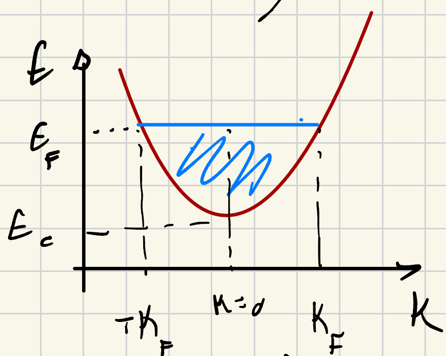
(Note that it's called r_s both dimensionless and none...)

* Ground state: N e^- fill in the N lowest states

. Spin ⇒ each state holds $2e^-$ (↑↓).



Real space



Reciprocal space

- Fermi Surface in $\vec{k}$ space given by $\epsilon(k) < \epsilon_F$ separates empty (unoccupied) & occ states.

- For Free e^- Fermi surface is a sphere of radius k_F

- k_F given by requirement that Total # of states $= N$

$$N = \sum_{\vec{k}}^{|k|<k_F} \underset{\text{spin}}{2} = \frac{V}{(2\pi)^3} \int d^3k \; 2 = \frac{2V}{(2\pi)^3} \frac{4}{3} \pi k_F^3 = \frac{V}{3\pi^2} k_F^3$$

$$\Rightarrow k_F = (3\pi^2 n)^{1/3}$$

- Using r_s : $\boxed{k_F = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s \cdot a_B}}$

- Taking $\vec{p} = \hbar \vec{k}$ we can also define a Fermi velocity

$$\vec{V}_F = \frac{\hbar}{m} \vec{k}_F$$

* Fermi Energy : $\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m a_B^2} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s^2}$

+ We can now compute the total energy of the free e^- gas as:

$d^3k = 4\pi k^2 dk$

$$E_0 = 2\sum_{k}^{|k|<k_F} \frac{\hbar^2 k^2}{2m} = 2\frac{V}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 \frac{\hbar^2 k^2}{2m} dk =$$

$$= 8\pi \frac{V}{(2\pi)^3} \frac{\hbar^2}{2m} \frac{k_F^5}{5}$$

as $N = \frac{V}{3\pi^2} k_F^3$ the energy/e^- is

$$\frac{E_0}{N} = \frac{*}{V/3\pi^2 \, k_F^3} = \frac{3}{5}\frac{\hbar^2}{2m} k_F^2 = \frac{3}{5} E_F$$

+ We can compute the Density of states from the dispersion relation $E_k = \frac{\hbar^2 k^2}{2m}$

$$D(E) = 2\frac{V}{(2\pi)^3}\int \delta\left(E - \frac{\hbar^2 k^2}{2m}\right) d^3k$$

$$= \frac{2V}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 \delta\left(E - \frac{\hbar^2 k^2}{2m}\right) dk$$

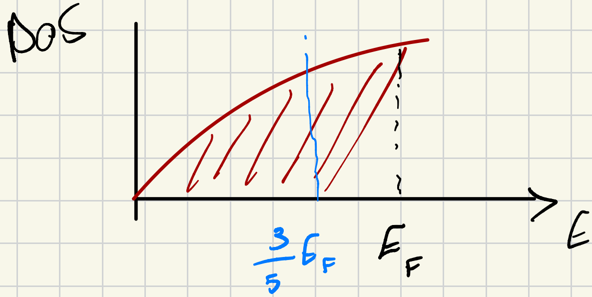
$$\hookrightarrow \delta[f(x)] = \sum_{x_0 \in \text{zeros of } f} \frac{\delta(x-x_0)}{|f'(x_0)|}$$

since $k_0 = \pm\sqrt{\frac{2mE}{\hbar^2}}$, $\frac{1}{|f'(k_0)|} = \frac{m}{\hbar^2 |k_0|}$

only + in integration range

$$D(E) = \frac{2V}{(2\pi)^3} 4\pi \left(\frac{2mE}{\hbar^2} \frac{m}{\hbar^2} \frac{\hbar}{\sqrt{2mE}} \right) = \frac{V\,(2m)^{3/2}}{2\pi^2 \hbar^3} E^{1/2}$$

* DOS for free e^- gas in 3D



- What about finite T?

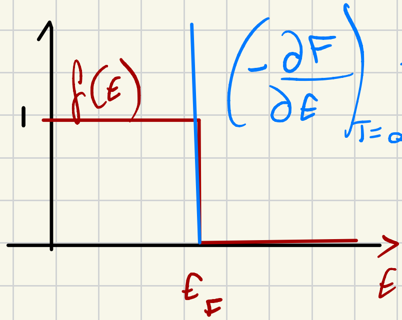
  . Identical Fermions $\Rightarrow$ Fermi-Dirac distribution gives occupation probability Vs T

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

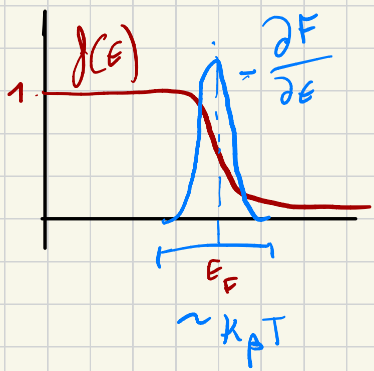
$\leftarrow$ Note here E_F is $E_F(T)$
E_F above is $E_F(T=0)$
usually $E_F(T) = \mu$
(chemical potential)

$$\frac{\partial F}{\partial E} = -\frac{e^{(E-E_F)/k_\beta T}}{\left[e^{(E-E_F)/k_\beta T}+1\right]^2}\frac{1}{k_\beta T} \quad \leftarrow \text{useful fn}$$

- For $T=0$ $\qquad\qquad\qquad\qquad$ $T>0$



$$\left(-\frac{\partial F}{\partial E}\right)_{T=0} = \delta(E-E_F)$$



* How does E_F change with T? $\left(E_F(T)=\mu\right)$

- Sommerfield expansion

→ Consider an integral with a generic smooth function $G(E)$ $\Rightarrow \displaystyle\int_{-\infty}^{\infty} G(E)\left(-\frac{\partial F}{\partial E}\right)dE$

→ Expand $G(E)$ around E_F

$$G(E) = G(E_F) + (E-E_F)\left.\frac{dG}{\partial E}\right|_{E=E_F} + \frac{1}{2}(E-E_F)^2\left.\frac{d^2G}{\partial E^2}\right|_{E=E_F} + \dots$$

$\rightarrow$ Integral Becomes:

$$\int_{-\infty}^{\infty} G(\epsilon)\left(-\frac{\partial F}{\partial \epsilon}\right) d\epsilon = G(\epsilon_F) + \frac{1}{2} \underbrace{G''(\epsilon_F)}_{\left.\frac{d^2G}{\partial \epsilon^2}\right|_{\epsilon=\epsilon_F}} \int_{-\infty}^{\infty} (\epsilon-\epsilon_F)^2 \left(-\frac{\partial F}{\partial \epsilon}\right) d\epsilon$$

where we used the fact that $\int_{-\infty}^{\infty}\left(-\frac{dF}{d\epsilon}\right) d\epsilon = -[\underbrace{f(\infty)}_{0} - \underbrace{f(-\infty)}_{1}] = 1$

And that odd powers give zero contribution since $-\frac{\partial f}{\partial \epsilon}$ is even around ϵ_F (a delta). So $(\epsilon-\epsilon_F)^{2m+1}\left(-\frac{\partial F}{\partial \epsilon}\right)$ is an odd fn around ϵ_F, integrating for $\epsilon\,[-\infty, \infty)$ vanishes.

- Coefficient of the G'' is:

$$\frac{1}{2}\int_{-\infty}^{\infty} (\epsilon-\epsilon_F)^2 \left(-\frac{\partial F}{\partial \epsilon}\right) d\epsilon = \frac{1}{2}\int_{-\infty}^{\infty} (\epsilon-\epsilon_F)^2 \underbrace{\frac{e^{(\epsilon-\epsilon_F)/k_BT}}{\left[e^{(\epsilon-\epsilon_F)/k_BT}+1\right]^2}}_{\text{Even FN}} \frac{1}{k_BT} d\epsilon$$

$$\frac{1}{2}\int_{-\infty}^{\infty} = \int_{0}^{\infty}$$

$$x = \frac{\epsilon-\epsilon_F}{k_BT} \qquad dx = \frac{d\epsilon}{k_BT}$$

$$\Rightarrow k_\beta^2 T^2 \int_0^{\infty} x^2 \frac{e^x}{(e^x+1)^2}\, dx = k_\beta^2 T^2 \frac{\pi^2}{6} \quad \left(\text{G.P sec III.2} \atop \text{A\&M ch.2}\right)$$

$$\text{So} \quad \int_{-\infty}^{\infty} G(\epsilon)\left(-\frac{\partial F}{\partial \epsilon}\right) d\epsilon = G(\epsilon_F) + G''(\epsilon_F)\, k_\beta^2 T^2 \frac{\pi^2}{6} + \dots$$

- Integrate the LHS by parts $\int u\,dv = uv - \int v\,du$

$$\int_{-\infty}^{\infty} G(\epsilon)\left(-\frac{\partial f}{\partial \epsilon}\right) d\epsilon = -G(\epsilon)\, F(\epsilon)\Big|_{-\infty}^{\infty} + \int_{-\infty}^{\infty} \frac{dG(\epsilon)}{d\epsilon} F(\epsilon)\, d\epsilon$$

assume $G(-\infty) = 0$

$G(+\infty)$ well behaved

$$G(\epsilon)\, F(\epsilon)\Big|_{-\infty}^{\infty} = 0$$

- In conclusion:

$$\int_{-\infty}^{\infty} \frac{dG(\epsilon)}{d\epsilon} f(\epsilon)\, d\epsilon = G(\epsilon_F) + \frac{\pi^2}{6} k_\beta^2 T^2 G''(\epsilon_F) + \dots$$

- Define $\Gamma(\epsilon)$ such that $G(\epsilon) = \int_{-\infty}^{\epsilon} \Gamma(\epsilon')\, d\epsilon'$

Then :

$$\boxed{\int_{-\infty}^{\infty} \Gamma(\epsilon) F(\epsilon)\, d\epsilon = \int_{-\infty}^{\epsilon_F} \Gamma(\epsilon)\, d\epsilon + \frac{\pi^2}{6}(k_\beta T)^2 \left.\frac{d\Gamma(\epsilon)}{d\epsilon}\right|_{\epsilon=\epsilon_F} + \mathcal{O}(T^4)}$$

Sommerfeld expansion

- Rapidly convergent. For example consider $G(\epsilon) = \epsilon^p$

$$\Rightarrow \text{Then} \int_{-\infty}^{\infty} \frac{dG(\epsilon)}{d\epsilon} F(\epsilon) = G(\epsilon_F) + \frac{\pi^2}{6} p(p-1)\left(\frac{k_\beta T}{\epsilon_F}\right)^2 G(\epsilon_F) + \ldots$$

polynomial

Terms decrease like $\left(\frac{k_\beta T}{\epsilon_F}\right)^{2n}$

- Use S.E on DOS at finite T

$$\int_{-\infty}^{\infty} D(\epsilon) F(\epsilon)\, d\epsilon = N = \int_{-\infty}^{\epsilon_F} D(\epsilon)\, d\epsilon + \frac{\pi^2}{6} k_\beta^2 T^2 \left.\frac{dD(\epsilon)}{\partial \epsilon}\right|_{\epsilon=\epsilon_F} + \ldots$$

↓ Differentiate both sides by T, using that

$$\frac{d}{db}\int_a^b f(x)\,dx = f(b)$$

$$\frac{d}{dT}\int_{-\infty}^{\epsilon_F(T)} D(\epsilon)\, d\epsilon = \frac{d\epsilon_F}{dT}\frac{d}{d\epsilon_F}\int_{-\infty}^{\epsilon_F(T)} D(\epsilon)\, d\epsilon = \frac{d\epsilon_F}{dT} D(\epsilon_F)$$

So:

$$\frac{dN}{dT} = 0 = \frac{d\epsilon_F}{dT} D(\epsilon_F) + \frac{\pi^2}{3} k_\beta^2 T \left.\frac{dD(\epsilon)}{dE}\right|_{\epsilon=\epsilon_F} + \dots$$

$$\Longrightarrow \boxed{\frac{d\epsilon_F}{dT} = -\frac{\pi^2}{3} k_\beta^2 T \frac{D'(\epsilon_F)}{D(\epsilon_F)}} \leftarrow D'(\epsilon_F) = \left.\frac{dD(\epsilon)}{d\epsilon}\right|_{\epsilon=\epsilon_F}$$

For 3D e^- gas $D(\epsilon) \propto \epsilon^{1/2}$ so:

$$\frac{D'(\epsilon_F)}{D(\epsilon_F)} = \frac{1/2 \; 1/\sqrt{\epsilon_F}}{\sqrt{\epsilon_F}} = \frac{1}{2\epsilon_F} \quad \text{and} \quad \frac{d\epsilon_F}{dT} = -\frac{\pi^2}{6} k_\beta^2 T \frac{1}{\epsilon_F}$$

$$\Downarrow$$

$$\epsilon_F \frac{d\epsilon_F}{dT} = -\frac{\pi^2}{6} k_\beta^2 T$$

$$\Downarrow$$

$$\frac{1}{2} \frac{d(\epsilon_F^2)}{dT} = -\frac{\pi^2}{6} k_\beta^2 T$$

Integrate Both sides:

$$\frac{1}{2} \int_0^T \frac{d}{dT'} \left(\epsilon_F^2\right) dT' = -\frac{\pi^2}{6} k_\beta^2 \int_0^T T' dT'$$

$$\Rightarrow \frac{1}{2}\left[\epsilon_F^2(T) - \epsilon_F^2(0)\right] = -\frac{\pi^2}{12} k_\beta^2 T^2 \Rightarrow \epsilon_F(T) = \sqrt{\epsilon_F^2(0) - \frac{\pi^2}{6} k_\beta^2 T^2}$$

$$= \epsilon_F(0) \sqrt{1 - \frac{\pi^2}{6} \frac{k_\beta^2 T^2}{\epsilon_F^2(0)}}$$

$$\Longrightarrow$$

$$\boxed{E_F(T) \simeq E_F(0)\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{E_F(0)}\right)^2\right]}$$ → Slow decrease of $E_F(T)$ vs T (Chemical potential decreases with T)

* Other properties of the free e^- gas:

Specific Heat: $C_v = \left.\frac{\delta Q}{\delta T}\right|_V$ • Extensive quantity (depends on system size)

change in internal energy U: $dU = \delta Q + \delta L$

Work done on system
$\delta L = -p\,dV$ if just mechanical work

$\delta L = 0$ if mechanical work

$$C_V = \left.\frac{dU}{dT}\right|_V$$

$$U(T) = \int_{-\infty}^{\infty} E\, D(E)\, F(E)\, dE$$

$$= \int_{-\infty}^{E_F} E\, D(E)\, dE + \frac{\pi^2}{6} k_B^2 T^2 \frac{d}{dE}\left[E\, D(E)\right]_{E_F} + \ldots$$

$$= \int_{-\infty}^{E_F} E\, D(E)\, dE + \frac{\pi^2}{6} k_B^2 T^2 \left[D(E_F) + E_F\, \dot{D}(E_F)\right]$$

So using $\frac{d}{dT}\int_{-\infty}^{E_F(T)} \epsilon\, D(\epsilon)\, d\epsilon = E_F\, D(E_F)\frac{dE_F}{dT}$

$$C_V = \frac{dU}{dT}\Big|_V = E_F\, D(E_F)\frac{dE_F}{dT} + \frac{\pi^2}{6}k_B^2 T^2\left[2T D(E_F) + 2T E_F D'(E_F) + \dots\right]$$

We know from before that $\frac{dE_F}{dT} = -\frac{\pi^2}{3}k_B^2 T\,\frac{D'(E_F)}{D(E_F)}$

$$C_V = \cancel{E_F\, D(E_F)\left[-\frac{\pi^2}{3}k_B^2 T\,\frac{D'(E_F)}{D(E_F)}\right]} + \frac{\pi^2}{3}k_B^2\left[T D(E_F) + \cancel{T E_F D'(E_F)}\right]$$

$$= \frac{\pi^2}{3}k_B^2\, T\, D(E_F)$$

• Since $D(E_F)$ is weakly T dependent, we can write

$$\boxed{C_V = \frac{\pi^2}{3}k_B^2\, T\, D[E_F(0)]}$$

Only electronic contribution to C_V (NOT lattice yet!).

DOS (3D) $\rightarrow D(\epsilon) = V\frac{(2m)^{3/2}}{2\pi^2\hbar^3}E^{1/2}$

$$\Rightarrow \boxed{C_V = \frac{\pi^2}{3} k_\beta^2 T \frac{3}{2} \frac{N}{\epsilon_F} = \frac{\pi^2}{2} k_\beta \frac{T}{T_F}}$$ ← only e^- around ϵ_F contribute to C_V

If heat is received as part of a reversible process in a closed system the 2nd Law of Thermodynamic states:

$$dS = \frac{dQ}{T} \qquad C_V = T \frac{dS}{dT}\Big|_V$$

$$\int_0^T \frac{dS}{dT} dT' = \int_0^T \frac{C_V}{T'} dT' = \int_0^T \frac{\pi^2}{3} k_\beta^2 D[\epsilon_F(0)] dT'$$

$$S(T) - \underbrace{\cancel{S(0)}}_{0} = \frac{\pi^2}{3} k_\beta^2 T D[\epsilon_F(0)] = C_V$$

$S = C_V \Rightarrow$ entropy of e^- system is the same as heat capacity.

Sommerfeld Th of Metals Summary

- Electrons fill in energy states up to fermi level

- At finite T, occupation of states is given by Fermi distribution

- Temperature dependence of properties or quantities like E_F, internal energy, C_V can be computed using Sommerfeld expansion.

  * E_F is weakly T dependent since $E_F \gg k_B T$

- Heat capacity is the same as entropy in the electronic system.