I.B : Sommerfeld theory of metals

- So far we have mostly considered a single electron interacting with a simple periodic potential
- Considering the more realistic situation of interacting electrons and nuclei of the crystal will be postponed for now
- We will consider a simpler case: Sommerfeld model

* Assume we have some "conduction" electrons in a metal
- We discussed a while ago that some electrons are tightly-bound to atoms while others may participate in bonding / conduction ("valence")

* Assume that these electrons feel a constant potential throughout the crystal:

$$\left[\frac{\vec{p}^{\,2}}{2m} + E_c\right]\psi(\vec{r}) = E\psi(\vec{r})$$

- All of the variations in crystal potential smeared out into constant E_c.
- Eigenfunctions are: $\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$
- Eigenvalues are: $E(\vec{k}) = \underbrace{E_c}_{\text{set to zero for simplicity}} + \frac{\hbar^2 k^2}{2m}$

* Consider now N free electrons in volume V. We often define election density with dimensionless parameter r_s:

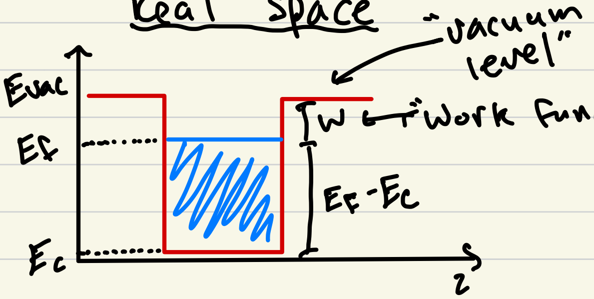
$$\frac{4}{3}\pi r_s^3 \underbrace{a_B^3}_{\text{Bohr radius}} = \underbrace{\frac{1}{n}}_{\text{density}} = \frac{V}{N}$$

* Ground state means accomodating N electrons into N lowest energy available states

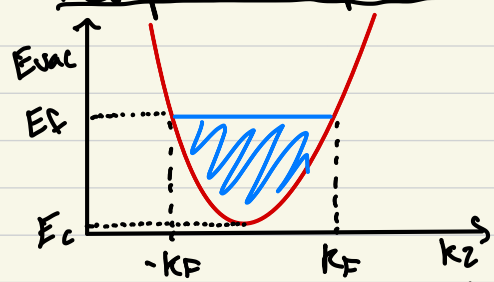
- Each state with wavevector $\vec{k}$, energy $E(\vec{k})$ can hold 2 electrons (up and down spin)

- States fill to Fermi energy E_F, Fermi wavevector k_F

Real space



Reciprocal space



- Fermi surface in $\vec{k}$ space given by $E(\vec{k}) < E_F$ separates occupied and unoccupied states

- For free electron case, Fermi surface is a sphere in reciprocal space of radius k_F

- k_F given by requirement that total number of states equals N:

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

for spin

$$\Rightarrow k_F^3 = 3\pi^2 \frac{N}{V} = 3\pi^2 n$$

- Using the definition of r_s:

$$k_F^3 = 3\pi^2\left(\frac{3}{4}\frac{1}{\pi r_s^3 a_B^3}\right) = \frac{9}{4}\frac{\pi}{r_s^3 a_B^3}$$

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

* Taking $p = \hbar k$, we can define a "Fermi velocity":

$$v_F = \frac{\hbar}{m} k_F$$

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

* We can then write the total energy of the free-electron gas as:

integrate over Fermi sphere

$$E_0 = 2 \sum_{\vec{k}}^{|k|<k_F} \frac{\hbar^2 k^2}{2m} = 2 \frac{V}{(2\pi)^3} \int_0^{k_F} 4\pi k^2 \frac{\hbar^2 k^2}{2m} dk = 8\pi \frac{V}{(2\pi)^3} \frac{\hbar^2}{2m} \frac{k_F^5}{5}$$

- Since $N = \dfrac{V}{3\pi^2} k_F^3$, energy per electron is:

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

* We can compute the DOS from the dispersion relation:

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

Recall $\delta[f(x)] = \sum\limits_{x_0 \in \text{ zeros of } f} \dfrac{\delta(x - x_0)}{|f'(x_0)|}$

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

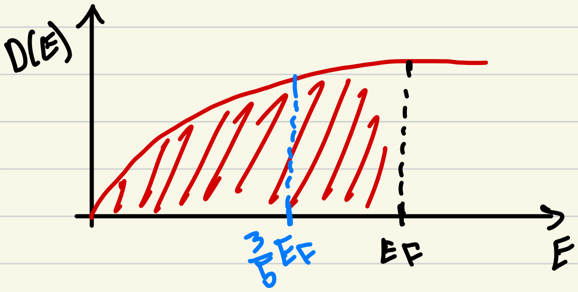
$$= \frac{2V}{(2\pi)^3} \int_0^{k_F} 4\pi k^2 \, \delta\left(E - \frac{\hbar^2 k^2}{2m}\right) dk$$

only + root in integration range

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

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

* DOS for free-electron gas:



- What about finite T?

* For an assembly of identical Fermions in thermal equilibrium, probability that one-particle state at energy E is occupied is Fermi-Dirac distribution:

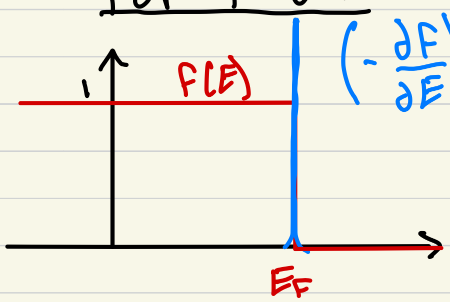
$$\boxed{f(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1}}$$

(see G and P Sec. III. Appendix B for derivation)

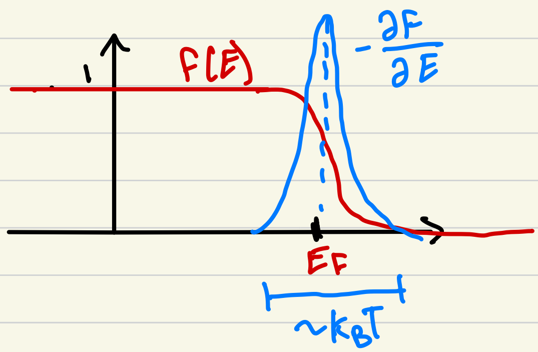
- $\frac{\partial f}{\partial E} = -\frac{e^{(E-E_F)/k_BT}}{\left[e^{(E-E_F)/k_BT} + 1\right]^2}\frac{1}{k_BT}$ is also a useful function (more later)

<u>For T=0:</u>

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



<u>For T>0:</u>



* How does E_F change w/ T?

- To calculate that, we perform Sommerfeld expansion
- Consider integral with a generic (smooth) function $G(E)$:

$$\int_{-\infty}^{\infty} G(E)\left(-\frac{\partial f}{\partial E}\right) dE$$

- Expand $G(E)$ around E_F:

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

- So integral becomes:

$$\int_{-\infty}^{\infty} G(E)\left(-\frac{\partial f}{\partial E}\right) dE = G(E_F) + \frac{1}{2}\underbrace{G''(E_F)}_{\left.\frac{d^2G}{dE^2}\right|_{E=E_F}}\int_{-\infty}^{\infty}(E-E_F)^2\left(-\frac{\partial f}{\partial E}\right) dE + \cdots$$

where we used the fact that $\int_{-\infty}^{\infty}\left(-\frac{\partial f}{\partial E}\right) dE = -[f(\infty)-f(-\infty)] = 1$

And that odd powers give zero contribution, since $-\frac{\partial f}{\partial E}$ is even around E_F, so $(E-E_F)^{2n+1}\left(-\frac{\partial f}{\partial E}\right)$ is an odd function around E_F, integral over all E vanishes.

- Coeff. of the G'' is:

$$\frac{1}{2}\int_{-\infty}^{\infty}(E-E_F)^2\left(-\frac{\partial f}{\partial E}\right) dE = \frac{1}{2}\int_{-\infty}^{\infty}(E-E_F)^2\frac{e^{(E-E_F)/k_BT}}{\left[e^{(E-E_F)/k_BT}+1\right]^2}\frac{1}{k_BT}\, dE$$

Change variables $(E-E_F)/k_BT \to x \qquad dx = \frac{dE}{k_BT}$

and use the fact that it is even function: $\frac{1}{2}\int_{-\infty}^{\infty} \to \int_0^{\infty}$

$$= k_B^2T^2\int_0^{\infty} x^2\frac{e^x}{(e^x+1)^2}\, dx = k_B^2T^2\,\frac{\pi^2}{6} \quad \left(\text{See G and P Sec III.2}\right)$$

So: $$\int_{-\infty}^{\infty} G(E)\left(-\frac{\partial f}{\partial E}\right) dE = G(E_F) + G''(E_F)\, k_B^2T^2\,\frac{\pi^2}{6} + \cdots$$

- In a similar way can get $G''''(E_F)$ term, etc.

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

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

Assume: $G(-\infty) = 0$
$G(\infty)$ well behaved

Then $G(E)f(E)\Big|_{-\infty}^{\infty} = 0$

- Therefore:

$$\int_{-\infty}^{\infty} \frac{dG(E)}{dE} f(E)\, dE = G(E_F) + \frac{\pi^2}{6} k_B^2 T^2 G''(E_F) + \cdots$$

- define $\Gamma(E)$ s.t. $G(E) = \int_{-\infty}^{E} \Gamma(E')\, dE'$

then:

$$\boxed{\int_{-\infty}^{\infty} \Gamma(E) f(E)\, dE = \int_{-\infty}^{E_F} \Gamma(E)\, dE + \frac{\pi^2}{6}(k_B T)^2 \left.\frac{d\Gamma(E)}{dE}\right|_{E=E_F} + \mathcal{O}(T^4)}$$

- known as Sommerfeld expansion
- Rapidly convergent. For example consider $G(E) \sim E^p$ i.e., polynomial type.

$\Rightarrow$ Then: $\int_{-\infty}^{\infty} \frac{dG(E)}{dE} f(E) = G(E_F) + \frac{\pi^2}{6} p(p-1)\left(\frac{k_B T}{E_F}\right)^2 G(E_F) + \cdots$

So terms decrease like $\left(\frac{k_B T}{E_F}\right)^{2n}$

$\Rightarrow$ E_F for most metals is ~ 10 eV, $k_B T \sim 0.026$ eV

- Now lets use Sommerfeld expansion on DOS at finite T:

$$\int_{-\infty}^{\infty} D(E) f(E)\, dE = N = \int_{-\infty}^{E_F} D(E)\, dE + \frac{\pi^2}{6} k_B^2 T^2 \left.\frac{dD(E)}{dE}\right|_{E=E_F} + \cancel{\mathcal{O}(T^4)}$$

neglect T^4 and higher terms

- Differentiate both sides by T, using that

$$\frac{d}{dT}\int_{-\infty}^{E_F(T)} D(E)\, dE = \frac{dE_F}{dT}\frac{d}{dE_F}\int_{-\infty}^{E_F(T)} D(E)\, dE = \frac{dE_F}{dT} D(E_F)$$

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

So:

$$\frac{dN}{dT} = 0 = \frac{dE_F}{dT} D(E_F) + \frac{\pi^2}{3} k_B^2 T \left.\frac{dD(E)}{dE}\right|_{E=E_F} + \cancel{\mathcal{O}(T^2)}$$

neglect

• So:

$$\boxed{\frac{dE_F}{dT} = -\frac{\pi^2}{3} k_B^2 T \frac{D'(E_F)}{D(E_F)}}$$

$D'(E_F) = \left.\frac{dD(E)}{dE}\right|_{E=E_F}$

• For 3D free electron gas, $D(E) \propto E^{\frac{1}{2}}$ so

$$\frac{D'(E_F)}{D(E_F)} = \frac{\frac{1}{2}\frac{1}{\sqrt{E_F}}}{\sqrt{E_F}} = \frac{1}{2E_F} \quad \text{and} \quad \frac{dE_F}{dT} = -\frac{\pi^2}{6} k_B^2 T \frac{1}{E_F}$$

$$E_F \frac{dE_F}{dT} = -\frac{\pi^2}{6} k_B^2 T$$

$$\frac{1}{2}\frac{d}{dT}(E_F^2) = -\frac{\pi^2}{6} k_B^2 T$$

Integrate both sides!

$$\frac{1}{2}\int_0^T \frac{d}{dT'}(E_F^2)\, dT' = -\frac{\pi^2}{6} k_B^2 \int_0^T T'\, dT$$

$$\Rightarrow \frac{1}{2}\left[E_F^2(T) - E_F^2(0)\right] = -\frac{\pi^2}{12} k_B^2 T^2$$

$$\Rightarrow \quad E_F(T) = \sqrt{E_F^2(0) - \frac{\pi^2}{6} k_B^2 T^2}$$

$$= E_F(0)\sqrt{1 - \underbrace{\frac{\pi^2}{6}\frac{k_B^2 T^2}{E_F^2(0)}}_{\text{small!}}}$$

$\sqrt{1-x} = 1 - \frac{x}{2} - \ldots$

$$\boxed{E_F(T) \approx E_F(0)\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{E_F(0)}\right)^2\right]}$$

↳ slow decrease in E_F as a function of T

- We can analyze other properties of the free electron gas

- Consider the heat capacity: $C_V = \left.\frac{\delta Q}{dT}\right|_V$

heat transferred from the environment (path/process function)

T increase of system (state function)

* Extensive quantity (depends on system size)

* Consider the change in internal energy U:

$$dU = \delta Q + \delta L$$

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

Therefore, $C_V = \left.\frac{dU}{dT}\right|_V$ ← constant V

$$U(T) = \int_{-\infty}^{\infty} \underbrace{E\,D(E)}_{\text{energy of state times DOS}}\, f(E)\, dE$$

$$= \int_{-\infty}^{E_F} E\,D(E)\,dE + \frac{\pi^2}{6}k_B^2T^2 \frac{d}{dE}\left[E\,D(E)\right]_{E_F} + \mathcal{O}(T^4)$$

$$= \int_{-\infty}^{E_F} E\,D(E)\,dE + \frac{\pi^2}{6}k_B^2T^2\left[D(E_F) + E_F\,D'(E_F)\right]$$

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

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

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

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

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

- since E_F is weakly T dependent, we can write

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

Fermi energy at $T=0$

- Note, only electron contribution to C_V (will discuss lattice contribution later)
- For free electron gas, DOS is $D(E) = V\dfrac{(2m)^{3/2}}{2\pi^2\hbar^3}E^{1/2}$

$$C_V = \frac{\pi^2}{3}k_B^2 T\,\frac{3}{2}\,\frac{N}{E_F}$$ number of e^- and $D(E_F) = \dfrac{3}{2}\dfrac{N}{E_F}$

Define $T_F = \dfrac{E_F}{k_B} \Rightarrow \boxed{C_V = \dfrac{\pi^2}{2}k_B\dfrac{T}{T_F}}$

only electrons around E_F contribute to C_V

* If the heat is recieved as part of a reversible process in a closed system, 2^{nd} law of thermodynamics states:

$$dS = \frac{\delta Q}{T} \quad \text{so} \quad C_V = T\left.\frac{dS}{dT}\right|_V$$

- So:

$$\int_0^T \frac{dS}{dT'}\,dT = \int_0^T \frac{C_V}{T'}\,dT' = \int_0^T \frac{\pi^2}{3}k_B^2\, D[E_F(0)]\, dT'$$

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

third law of thermodynamics

$\Rightarrow S = C_V$, entropy of electronic system is same as the heat capacity

Sommerfeld model of metals: What have we learned?

- Electrons are filled into energy states up to the Fermi energy.
- At finite temperature, the occupation of states is given by the Fermi distribution
- Temperature dependence of quantities like the fermi energy, internal energy, etc. can be estimated by Sommerfeld expansion
    * E_F is weakly T depenendent since usually $E_F >> k_B T$
- Heat capacity is the same as entropy in the electronic system.