3 Sommerfeld theory

Electrons = fermions ∴ Pauli Exclusion

3.1 1 Electron

- Energy: $H = \frac{p^2}{2m}$ $\quad \underbrace{\vec{p} = -i\hbar\vec{\nabla}_r}_{\text{quantum mechanics}}$
- Spin-$\frac{1}{2}$ basis state $|\vec{r}\uparrow\rangle$ and $|\vec{r}\downarrow\rangle$
- Periodic BC $\langle \vec{r}\sigma|\psi\rangle = \psi_\sigma(\vec{r}) = \psi_\sigma(\vec{r} + \vec{e}L)$

  $\vec{e} = \vec{x}, \vec{y}, \vec{z}$

Eigenenergies

$$H|\phi\rangle = E|\phi\rangle \qquad (\text{TDSE})$$

time dependent schrodinger eqn

+ write in position basis

$$\langle \vec{r}\sigma | H | \phi \rangle = E \langle \vec{r}\sigma | \phi \rangle$$

$$\Longrightarrow \quad -\frac{\hbar^2}{2m}\nabla_r^2 \phi_\sigma(\vec{r}) = E\phi_\sigma(\vec{r})$$

$$E(\vec{k}\sigma) = \frac{\hbar^2 k^2}{2m} \qquad \vec{k} = \frac{2\pi}{L}\vec{n} \qquad n_i = \text{integer}$$

solutions labelled by momentum

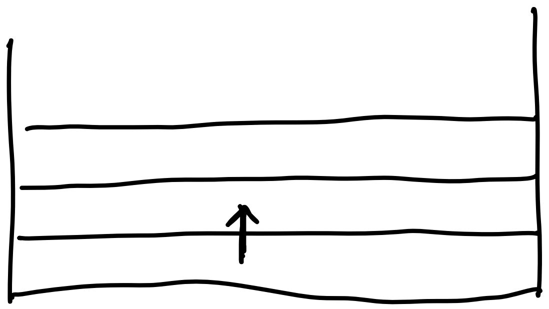
$$\phi_{\vec{k}\sigma}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \longrightarrow \text{normalisation}$$

denote $\langle \vec{r}\sigma | \vec{k}\tau \rangle = \delta_{\sigma\tau}\phi_{\vec{k}\tau}(\vec{r})$

Ground State

$$\vec{k} = 0 \Rightarrow \phi_{gs} = \frac{1}{\sqrt{V}} \qquad E_{gs} = 0$$

Box



3.2 - 2 Electrons

- State $\langle \vec{r}_1 \sigma_1 \vec{r}_2 \sigma_2 | \Psi \rangle = \Psi(\vec{r}_1, \sigma_1, \vec{r}_2 \sigma_2)$

- Energy $H = \sum_{n=1,2} \frac{p_n^2}{2m}$ $\quad \vec{p}_n = -i\hbar \vec{\nabla}_n$

$$= \sum_{n=1,2} \frac{\hbar^2 \vec{\nabla}_n^2}{2m}$$

- Periodic BC $\langle \vec{r}_1 \sigma_1 \vec{r}_2 \sigma_2 | \Psi \rangle$ unchanged for

$$\vec{r}_1 \to \vec{e}L, \quad \vec{r}_2 \to \vec{e}L$$

for $\vec{e} = \vec{x}, \vec{y}, \vec{z}$

- Fermions

let P be adiabatic particle exchange

$$(P\Psi)(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2) = \Psi(\vec{r}_2\sigma_2, \vec{r}_1\sigma_1)$$

$$\therefore P^2\Psi = \Psi \qquad * \ (D>2)$$

double swap does nothing

we are being a bit crude — these args only work if we have a single swap operator

assert definite symmetry

$$P\Psi = \lambda\Psi$$

$$\therefore P^2\Psi = \lambda^2\Psi = \Psi$$

$$\lambda = \begin{cases} +1 & \text{bosons} \\ -1 & \text{fermions} \end{cases}$$

$$\Psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2) = -\Psi(\vec{r}_2\sigma_2, \vec{r}_1\sigma_1)$$

→ antisymmetric under particle exchange

→ cannot have a simple product state

$$\Psi(r_1\sigma_1\, r_2\sigma_2) \neq \langle r_1\sigma_1 | k_1\tau_1\rangle \langle r_2\sigma_2 | k_2\tau_2\rangle$$

→ violates the exchange symmetry

→ simplest allowed form is

$$\Psi(r_1\sigma_1\, r_2\sigma_2) = \frac{1}{\sqrt{2}}\Big[\langle r_1\sigma_1|k_1\tau_1\rangle\langle r_2\sigma_2|k_2\tau_2\rangle - \langle r_1\sigma_1|k_2\tau_2\rangle\langle r_2\sigma_2|k_1\tau_1\rangle\Big]$$

$$= \frac{1}{\sqrt{2!}} \det\Big[\langle r_n\sigma_n|k_m\tau_m\rangle\Big]_{n,m=1}^{2}$$

$$\det\begin{pmatrix} a & b \\ c & d \end{pmatrix} = ab - dc$$

Note

$$\Psi = 0 \quad \text{if} \quad (k_1\tau_1 = k_2\tau_2) \;\text{or}\; (r_1\sigma_1 = r_2\sigma_2)$$

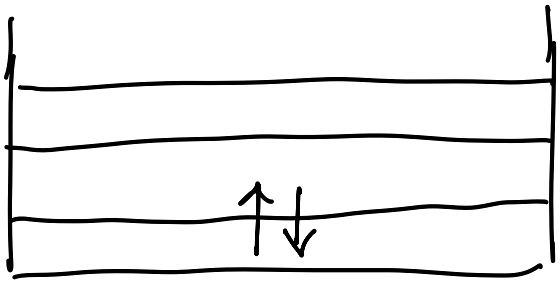
Eigenvalue

$$E(\vec{k}_1\sigma, \vec{k}_2\sigma_2) = \frac{\hbar^2}{2m}\left(k_1^2 + k_2^2\right)$$

→ find is eigenstate with

Ground state

$k_1 = k_2 = 0 \quad \sigma_1 \sigma_2 = \uparrow\downarrow$



3.3 N electrons

Slater determinants:

$$\langle \vec{r}_1 \sigma_1 \dots \vec{r}_N \sigma_N | \Psi \rangle = \frac{1}{\sqrt{N!}} \det \left[\langle r_n \sigma_n | k_m \tau_m \rangle \right]_{n,m=1}^{N}$$

antisymmetric for any 2 electron exchange

$$\Psi(\dots \vec{r}_i \dots \vec{r}_j \dots) = - \Psi(\dots \vec{r}_j \dots \vec{r}_i \dots)$$

is eigenstate if

for all

$$(\tau_n \vec{k}_n) \neq (\tau_m \vec{k}_m) \quad \forall \; n, m$$

0 otherwise

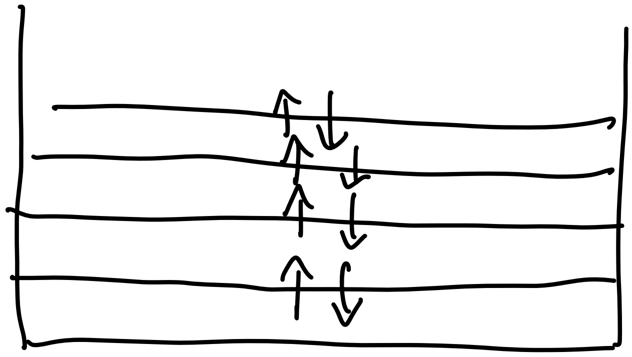
$$E = \frac{\hbar^2}{2m} \sum_n k_n^2 \quad \leftarrow$$

where each k-value can appear only twice

Conclusion

- Each orbital has max 1 electron

- Each k-mode has max 2 electrons $(\uparrow, \downarrow)$



- To find ground state we fill orbitals from low energy to high energy.

3.4 Finite temp

- Established how to find $|GS\rangle$
  → What about finite T

- Work at fixed chem potential μ
  → Grand canonical ensemble
  → Fixed (T, V, μ)

- $$Z = \sum_{\text{configs } c} e^{-\beta(E_c - \mu N_c)}$$

for non-interacting electrons

$$n_{k\sigma} = 0, 1 \qquad \forall\, k, \sigma$$

$$\therefore \quad E_c = \sum_{k\sigma} \epsilon_{k\sigma} n_{k\sigma} \qquad \epsilon_{k\sigma} = \frac{\hbar^2 k^2}{2m}$$

$$N_c = \sum_{k\sigma} n_{k\sigma}$$

∴ By direct calculation

$$\mathcal{Z} = \sum_{\{n_{k\sigma}\}} e^{-\beta \sum_{k\sigma} (\epsilon_{k\sigma} - \mu) n_{k\sigma}}$$

$$= \prod_{k\sigma} \sum_{n_{k\sigma}=0,1} e^{-\beta(\epsilon_{k\sigma} - \mu) n_{k\sigma}}$$

$$= \prod_{k\sigma} \left(1 + e^{-\beta(\epsilon_{k\sigma} - \mu)}\right)$$

∴ Electron number

$$N = kT \frac{\partial \log Z}{\partial \mu} = \sum_{k\sigma} f_{k\sigma}$$

where $f_{k\sigma} = f_{FD}(\beta(\epsilon_{k\sigma} - \mu))$

$$f_{FD} = \frac{1}{e^{x} + 1}$$

∴

$$\therefore \quad U = -\frac{\partial \log Z}{\partial \beta} + \mu N = \sum_{k\sigma} f_{k\sigma} \epsilon_{k\sigma}$$

- Last Class

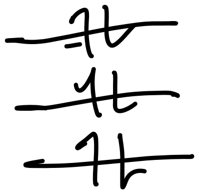
  - Considered particle statistics

Exchange antisym $\Longrightarrow$ Pauli Exclusion

(Fermions) (1 electron per state)

definition of fermion

$$\psi(r_1 r_2) = -\psi(r_2 r_1)$$



spin ↑ + spin ↓ different states

(T=0)

  - Construct non interacting ground state

Non interacting H $\Longrightarrow$ Slater determinant

$$H = \sum_{n=1}^{N} H_{sp}(\vec{r}_n \sigma_n)$$

$$= \sum_{n=1}^{N} \frac{p_n^2}{2m^*}$$

electron effective mass

→ turns out this model is going to be useful more useful if we allow $m \to m^*$

- Construct Eqm state $(T > 0)$

→ use grand canonical partition function:

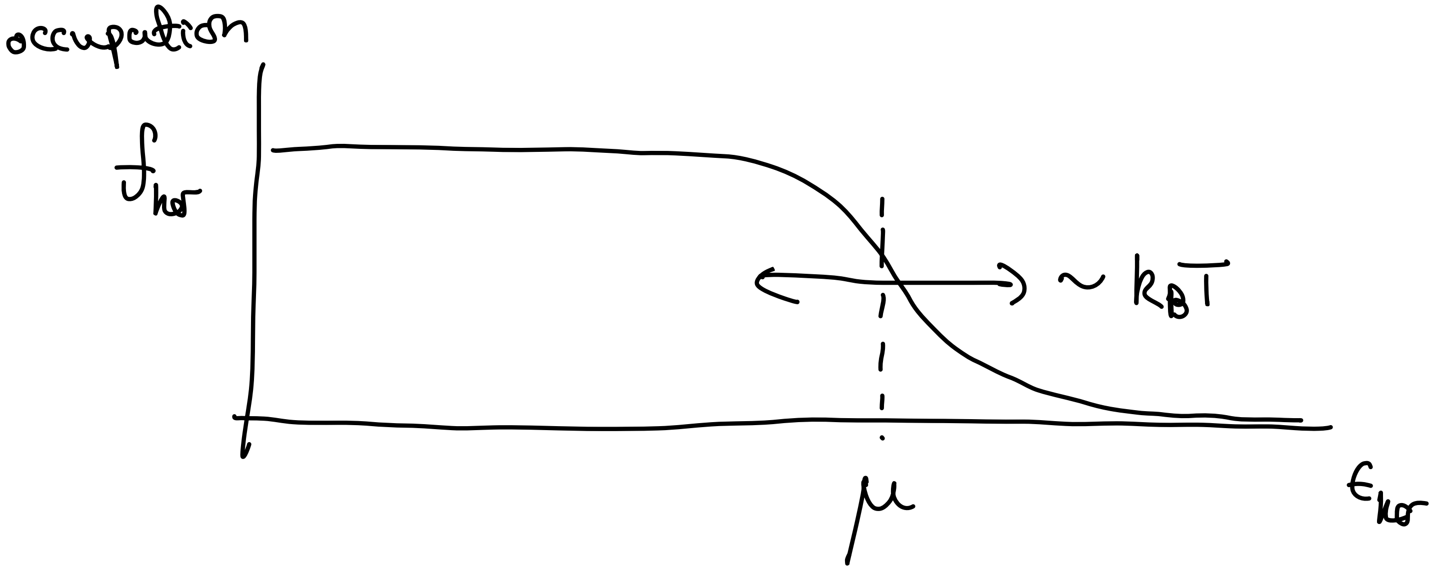
e in state $|k,\sigma\rangle$ $= \langle n_{k\sigma} \rangle = f_{k\sigma} = f_{FD}(\beta(\epsilon_{k\sigma} - \mu))$

$$f_{FD}(x) = \frac{1}{e^x + 1}$$

equilibrium # electrons in the state $|k,\sigma\rangle$

$$N = \sum_{k\sigma} f_{k\sigma}$$

$$U = \sum_{k\sigma} f_{k\sigma} \epsilon_{k\sigma}$$

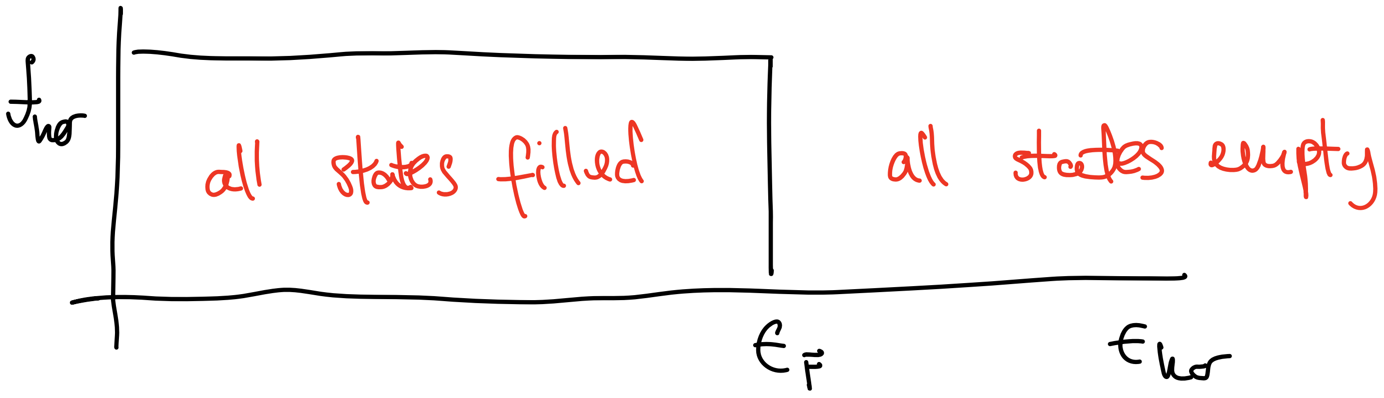


$$f_{k\sigma} = \begin{cases} 1 & \epsilon_{k\sigma} \ll \mu - k_B T \\ 0 & \epsilon_{k\sigma} \gg \mu + k_B T \end{cases}$$

3.5 Fermi surface

$$\epsilon_F = \lim_{T \to 0} \mu(T)$$

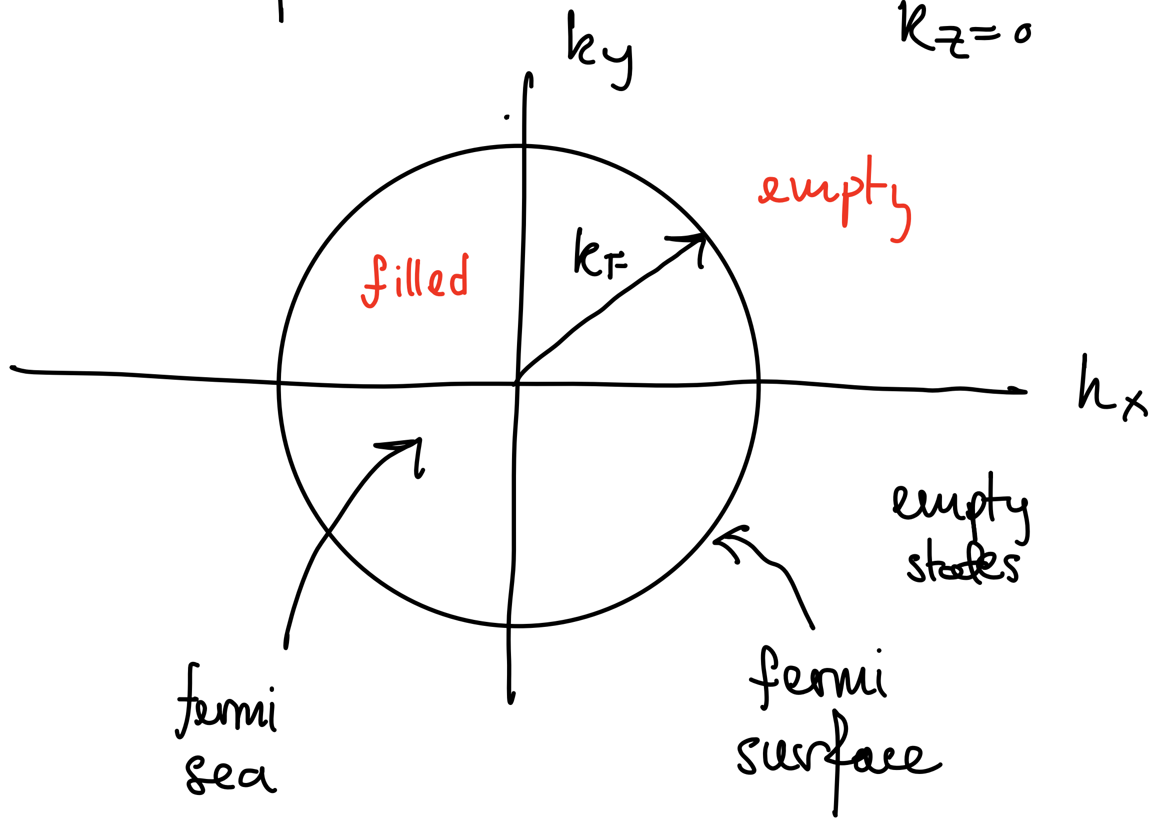
= single particle energy of most energetic electrons @ $T=0$.



various fermi surface properties

eg k_F : $\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$ fermi wavevector

in k-space



V_F : $\frac{1}{\hbar}\frac{\partial\epsilon}{\partial k}\Big|_{\epsilon=\epsilon_F}$ fermi velocity

T_F : $\epsilon_F = k_B T_F$ fermi Temp

these determine $T=0$ properties

$$N = \sum_{k\sigma} f_{k\sigma} = \underset{\overset{\uparrow}{\sum_\sigma}}{2}\, \underbrace{\frac{V}{(2\pi)^3}\int d^3k}_{\sum_k}\, \underbrace{\theta(\epsilon_F - \epsilon_k)}_{f_{k\sigma}}$$

$$= \frac{V}{\pi^2}\int_0^{k_F} dk\, k^2 = \frac{V k_F^3}{3\pi^2}$$

a simple intuition

let $\frac{4}{3}\pi r_s^3 = \frac{V}{N_{atoms}} = \frac{ZV}{N}$

$r_s =$ Wigner Seitz radius

↑ volume of a ball that contains on avg 1 electron

1.92...

$$\therefore\ r_s = \left(\frac{3ZV}{4\pi N}\right)^{1/3} = k_F^{-1}\left(\frac{9\pi Z}{4}\right)^{1/3}$$

$$\boxed{k_F^{-1} \sim r_s \sim \text{typical distance between electrons}}$$

specifically $k_F \sim 0.5 - 2\,\text{Å}^{-1}$, $m_* \sim m_e$

$$\therefore\ \epsilon_F \sim \frac{\hbar^2 k_F^2}{2m^*} \sim 1 - 16\ \text{eV}$$

$$T_F \sim \frac{\epsilon_F}{k_B} \sim 10^5 - 10^6\ \text{K}$$

$$V_F \sim \frac{\hbar k_F}{m^*} \sim 0.5 - 2 \times 10^6 \, m/s$$

$$\sim 0.01c$$ 1% speed of light!

→ electrons in a metal are <u>forced</u> to go at a non negligible frac of speed of light

3.6 Ground State Energy

E_F sets the typical kinetic energy of an electron in the ground state

Energy

$$U = \sum_{k\sigma} f_{k\sigma} \epsilon_{k\sigma}$$

$$\therefore U_0 = \frac{2V}{(2\pi)^3} \int d^3k \, \epsilon_{k\sigma} \Theta(\epsilon_F - \epsilon_k)$$

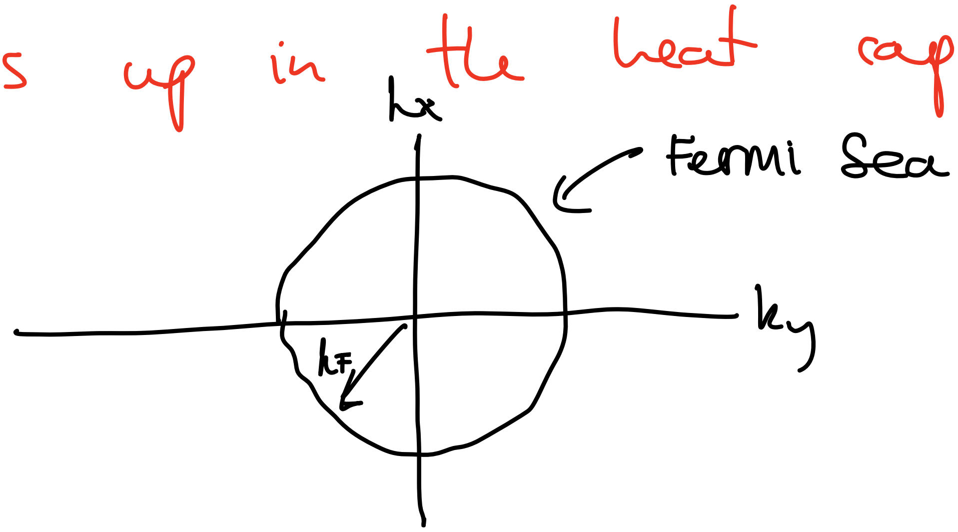
$$= \frac{V}{\pi^2}\int_0^{k_F} dk\, k^2 \cdot \left(\frac{\hbar^2 k^2}{2m}\right)$$

$$= \frac{V}{\pi^2}\cdot\frac{\hbar^2}{2m}\cdot\frac{k_F^5}{5}$$

$$\therefore \frac{U_0}{N} = \frac{3}{5}\,\frac{\hbar^2 k_F^2}{2m} = \frac{3}{5}E_F$$

- this is the ground state kinetic energy per electron — this energy cannot be extracted

- why do we care about what is extracted — because that's what shows up in the heat capacity



3.7 Electronic Heat Capacity

$$U(T) = \sum_{k\sigma} f_{k\sigma} \epsilon_{k\sigma}$$

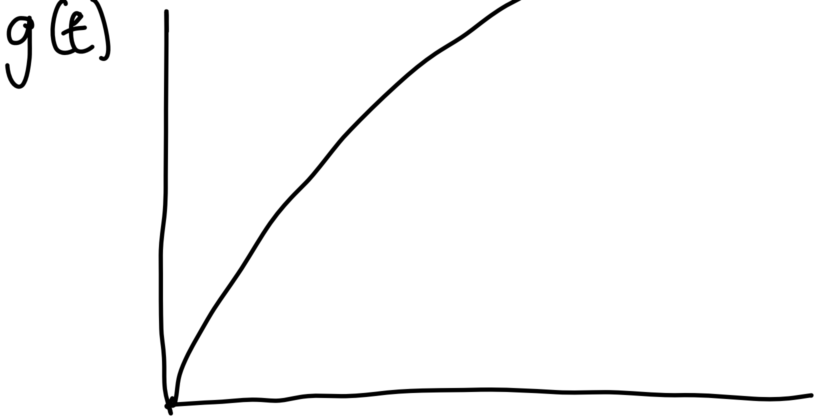
$$\sum_{k\sigma} \to \frac{2V}{(2\pi)^3}\int d^3k = \frac{V}{\pi^2}\int dk\, k^2 = \frac{V}{\pi^2}\int_{-\infty}^{\infty} d\epsilon \frac{dk}{d\epsilon}\left(\frac{2m\epsilon}{\hbar^2}\right)$$

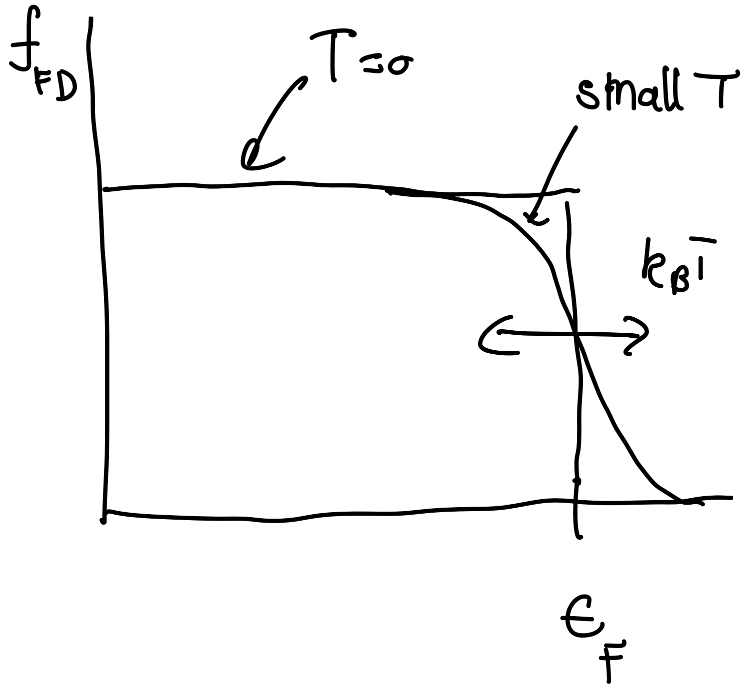
$$u = \frac{U}{N} = \int_{-\infty}^{\infty} d\epsilon\, g(\epsilon)\, f_{FD}(\beta(\epsilon-\mu))\, \epsilon$$

Where $g(\epsilon)$ is DOS ← electronic density of states

$$g(\epsilon<0) = 0$$

$$g(\epsilon>0) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\epsilon} = \frac{3n}{2\epsilon_F}\sqrt{\frac{\epsilon}{\epsilon_F}})$$





∴ # electrons excited ~ $V \cdot g(\epsilon_F) \cdot \Delta\epsilon = V g_F k_B T$

typical excitation energy per electron ~ $k_B T$

$$\therefore \Delta U \sim V g_F (k_B T)^2$$

density of electrons $n = \frac{N}{V} \sim k_F^3 = \left(\frac{2m\epsilon_F}{\hbar^2}\right)^{3/2}$

DOS at Fermi surface $g_F = \frac{3n}{2\epsilon_F}$

$$\Delta U_{mol} = \underset{\substack{\uparrow \\ \text{\# atoms} \\ \text{in mol}}}{N_A} \cdot \underset{\substack{\uparrow \\ \text{e per} \\ \text{atom}}}{Z} \cdot \underset{\substack{\uparrow \\ \text{energy per} \\ \text{electron}}}{\frac{\Delta U}{N}}$$

$$\sim N_A Z \cdot \frac{V g_F (k_B T)^2}{V n}$$

$$N_A Z \cdot \frac{3n}{2\epsilon_F} \cdot \frac{1}{n} (k_B T)^2$$

$$C_{el-mol} = \frac{d\Delta U_{mol}}{dT} = \frac{3}{2} R \overset{\substack{\text{electrons per} \\ \text{ion} \\ \swarrow}}{Z} \left(\frac{T}{T_F}\right)$$

if you do this much more carefully

→ make this a homework problem

$$C_{el-mol} = \frac{\pi^2}{2} R Z \frac{T \leftarrow 300K}{T_F \leftarrow 10^5 - 10^6 K} \quad \therefore \frac{T}{T_F} \sim 10^{-4}$$

compare with Maxwell - Boltzmann

$$\frac{U_{el}}{N_{el}} = \frac{3}{2} k_B T \longrightarrow C_{el-mol} = \frac{3}{2} R Z$$

off by about 4 orders magnitude!

naively T_F can be directly calculated

$$T_F = \frac{\epsilon_F}{k_B}, \quad \epsilon_F = \frac{\hbar^2 k_F^2}{2m^*} \quad k_F^3 = 3\pi^2 n \quad n = Z n_{atom} = \frac{Z\rho}{m_{atom}}$$

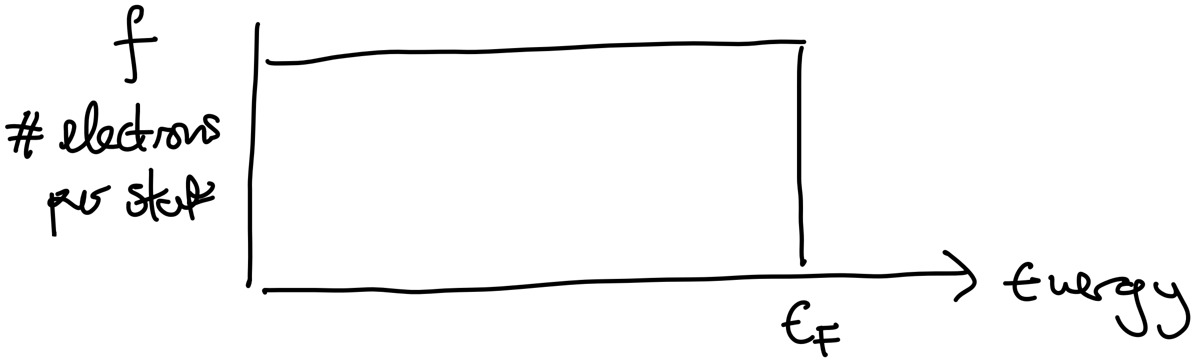
however agreement is best when m^* is treated as a fit parameter

→ useful to have another prediction to verify

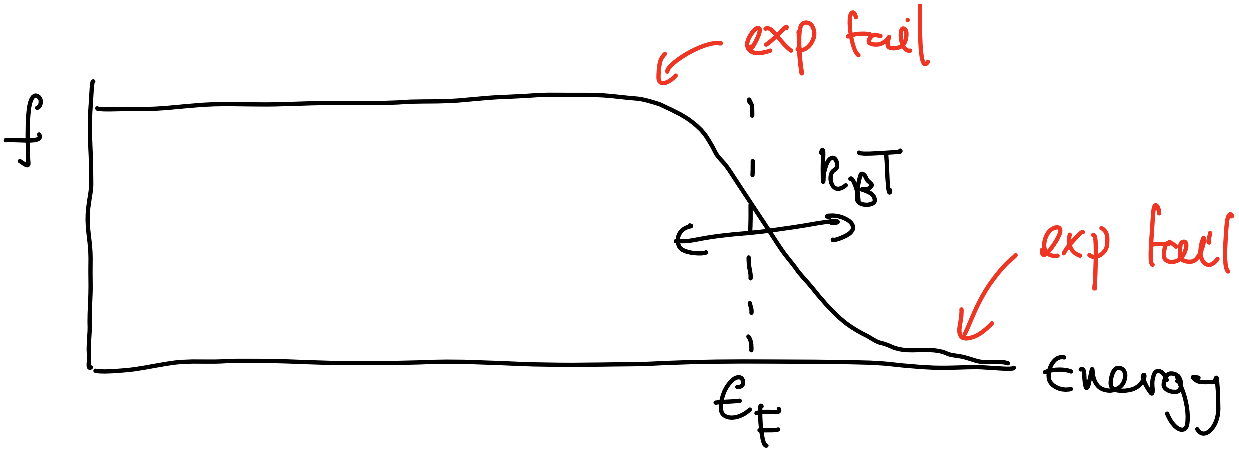
Last class

* Coopers question $\psi(r_1, r_2, r_3) = \psi(r_2 r_3 r_1)$

- Fermi sea ground state



- thermal excitations above the Fermi sea

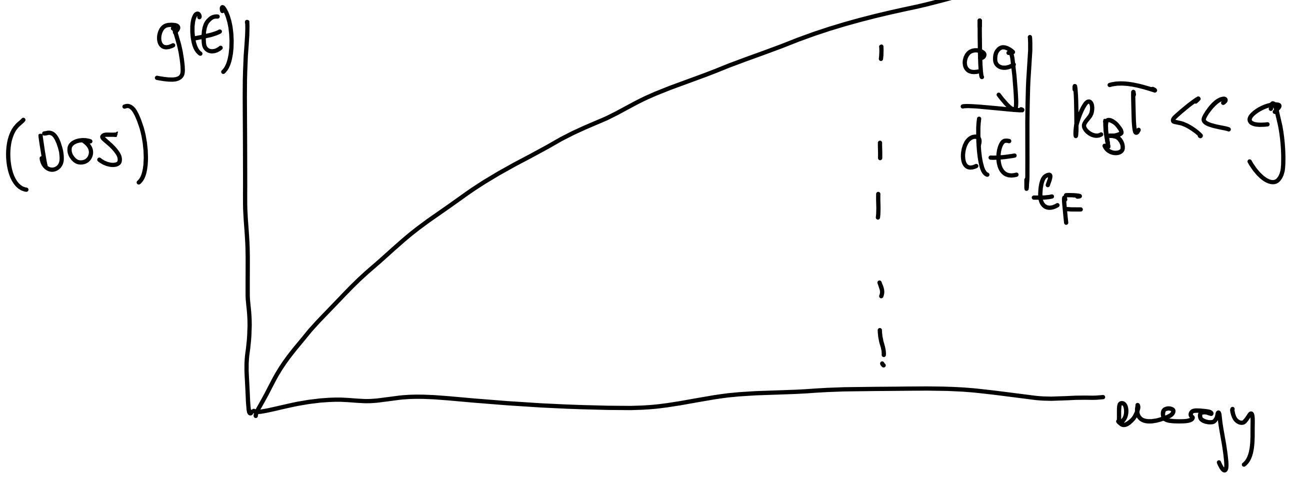


- change in occupation

only electrons within $k_B T$ of FS can excite

- Heat capacity

only other ingredient is DOS



$$\left.\frac{dg}{d\epsilon}\right|_{\epsilon_F} k_B T \ll g(\epsilon_F)$$

$$\Delta U \simeq (\#\ \text{ecited electrons}) \times (\text{avg. excitation energy})$$

$$\simeq \quad g(E_F)\,k_B T \quad \times \quad k_B T$$

$$C_{el\text{-}mol} = \frac{d\Delta U}{dT} \simeq \frac{3}{2} R Z \left(\frac{T}{T_F}\right) \qquad T_F = \frac{E_F}{k_B} \sim 10^5\text{-}10^6\,K$$

$R = N_A k_B$

$Z = e^-$ per atom

$\times 10^4$ smaller than MB $C_{el\text{-}mol} = \frac{3}{2} R Z$

more careful calculation

$$C_{el-mol} = \frac{\pi^2}{2} R Z \left(\frac{T}{T_F}\right)$$

$$T_F = \frac{E_F}{k_B} = \frac{\hbar^2}{2m^* k_B}\left(3\pi^2 n\right)^{2/3}$$

$\uparrow$ depends on m^*

often written as $C_{el-vol} = \gamma T + \ldots$

γ = Sommerfeld coefficient $= \frac{\pi^2}{3} k_B^2 \, g(E_F)$

- for some metals $m^* \simeq m_e$
- for others it can be v. different
- just like τ in drude theory we have a lingering dependence on a modelling parameter m^*

$$N = \frac{2V}{(2\pi)^3} \cdot \frac{4}{3}\pi k^3 = \frac{Vk^3}{3\pi^2}$$

↑

$$k_x = \frac{2\pi n_x}{L}$$

$$d^3k = \frac{(2\pi)^3}{V} d^3n$$

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

↙

$$g(E) = \frac{1}{V}\frac{dN}{d\epsilon} = \frac{1}{V}\frac{dN}{dk}\frac{dk}{d\epsilon} = \frac{k^2}{\pi^2} \cdot \frac{m^*}{k\hbar^2} = \frac{m^* k}{\pi^2 \hbar^2}$$

$$g(E_F) = \frac{m^*}{\pi^2\hbar^2}\left(3\pi^2 n\right)^{1/3}$$

↶ just $\frac{N}{V} = n = \frac{k^3}{3\pi^2}$

3.9 Paramagnetic Suceptibility

What: magnetic linear response

$$\underset{\substack{\uparrow \\ \text{response} \\ \to \text{magnetisation}}}{M} = \chi \underset{\substack{\uparrow \\ \text{applied field} \\ \to \text{external H-field}}}{H}$$

Paramagnetic $\Longrightarrow$ $\chi > 0$ and $M\big|_{H=0} = 0$

Dipolar field coupling

→ H is the field you set in magnetostatics, B is the field e^- sees

$$H = \underbrace{\frac{p^2}{2m^*}}_{\text{kinetic energy}} - \underbrace{\vec{\mu} \cdot \vec{B}}_{\text{dipole-field interaction}}$$

note B-field

$\vec{\mu}$ = electron dipole moment $= -\dfrac{g_e \mu_B}{\hbar} \vec{S}$

$\vec{S}$ = electron spin $= \dfrac{\hbar}{2} \vec{\sigma}$

$\vec{\sigma}$ = pauli matrices $\therefore \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ etc...

μ_B = Bohr magneton $= \dfrac{e\hbar}{2m_e}$

g_e = electron g-factor ≈ 2.002 in vacuum

$\simeq 2$

$$\therefore\ \epsilon_{\vec{k}\sigma} = \frac{\hbar^2 k}{2m} + \overbrace{\sigma\mu_B B}^{\text{zeeman splitting}}$$

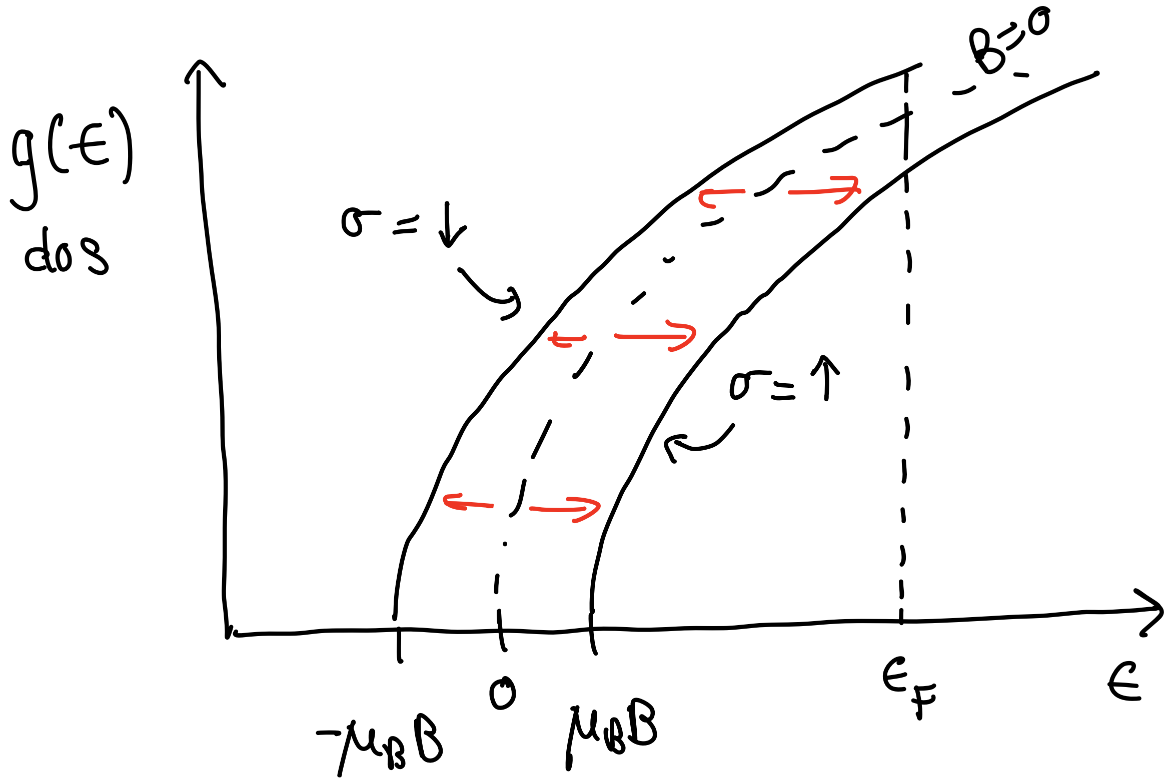
$\sigma = \pm 1 = \uparrow,\downarrow$

↑

$B\sigma$ is eigenvalue of $\vec{B}\cdot\vec{\sigma}$

$$= \underbrace{\epsilon_{k\sigma}\big|_{B=0} + \sigma\mu_B B}_{\text{simple spin dependent shift}}$$

Density of states



$$g_\sigma(\epsilon) = \frac{1}{2}\, g_0\underbrace{(\epsilon - \sigma\mu_B B)}_{B=0}$$

Density of spins in $\sigma = \uparrow\downarrow$

$$n_\sigma = \int_{-\infty}^{\epsilon_F} d\epsilon \; g_\sigma(\epsilon)$$

$$= \frac{1}{2}\int_{\sigma\mu_B B}^{\epsilon_F} d\epsilon \; g(\epsilon - \sigma\mu_B B)$$

$$= \frac{1}{2}\int_{0}^{\epsilon_F - \sigma\mu_B B} d\epsilon' \; g(\epsilon')$$

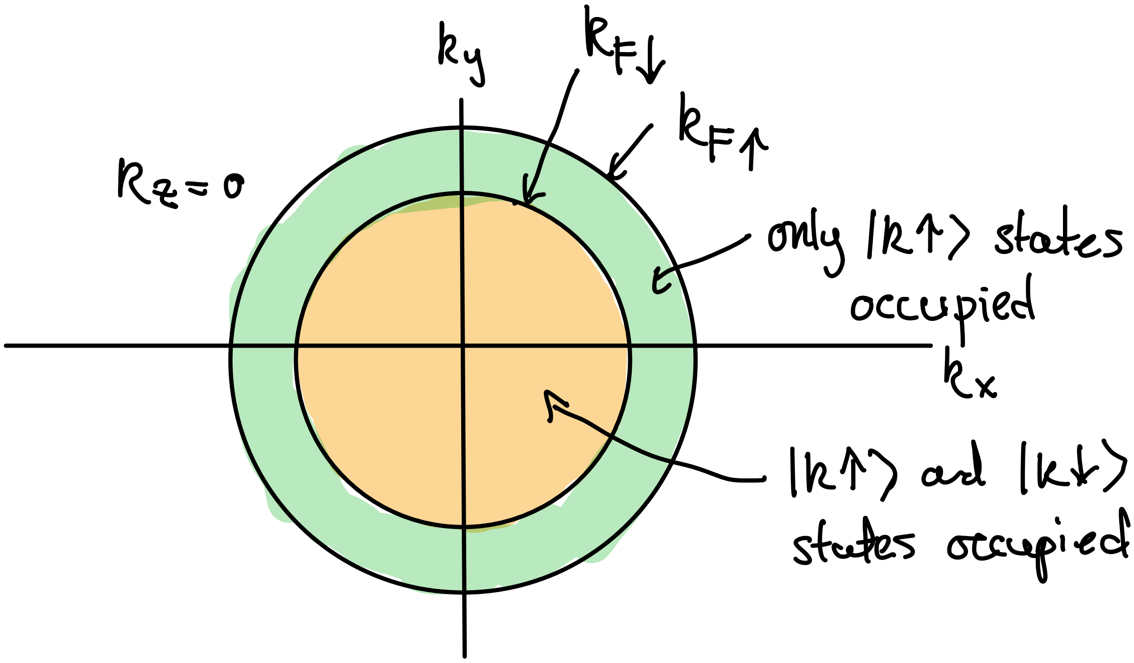
$$= \frac{1}{2}\left(n - \sigma\mu_B B\, g(\epsilon_F)\right) + O(B^2)$$

$$\therefore \quad n_\uparrow + n_\downarrow = n \quad \checkmark$$

havent broken anything

$$\text{but} \quad n_\uparrow \neq n_\downarrow$$

Picture: $k_z = 0$



magnetic moment per electron

$$m = -\mu_B (n_\uparrow - n_\downarrow) = \mu_B^2 g(\epsilon_F) B + O(B^2)$$

$$\therefore \chi_{pauli} = \frac{\partial m}{\partial H}\bigg|_{H=0} = \mu_0 \frac{\partial m}{\partial B}\bigg|_{B=0} = \mu_0 \mu_B^2 g(\epsilon_F)$$

$$m = \frac{M}{N} \quad B = \frac{H}{\mu_0}$$

recall sommerfeld coefficient

$$\gamma = \frac{\pi^2}{3} k_B^2 \, g(E_F)$$

Both depend on $g(\epsilon_F) \rightarrow$ depends on m^*

Ration - $g(E_F)$ independent

Define Wilson Ratio

$$R_W = \frac{\pi^2 k_B^2}{3\mu_0 \mu_B^2} \cdot \frac{\chi}{\gamma}$$

$R_W = 1$ Sommerfeld prediction

3.10 Comparison with Lorentz Gas

Lorentz Gas distribution function

$$N = \int d^3p \int d^3r\, f_{mB}(r, p)$$

$$= \frac{1}{(2\pi)^3} \int d^3k \int d^3r\, f_{MB}(r, k)$$ absorb $\hbar^3$ into f pull out $\frac{1}{(2\pi)^3}$

$$f_{MB} = n \left(\frac{2\pi\hbar^2}{mk_BT} \right)^{d/2} e^{-\frac{\hbar^2 k^2}{2mk_BT}}$$

writing the sommerfeld result in the same form

$$N = \frac{V}{4\pi^3} \int d^3k\, f_{FD}(\beta(\epsilon_k - \mu))$$

$$V = \int d^3r$$

$$= 2 \frac{1}{(2\pi)^3} \int d^3r \int d^3k \, f_{FD}\left(\beta(\epsilon_k - \mu)\right)$$

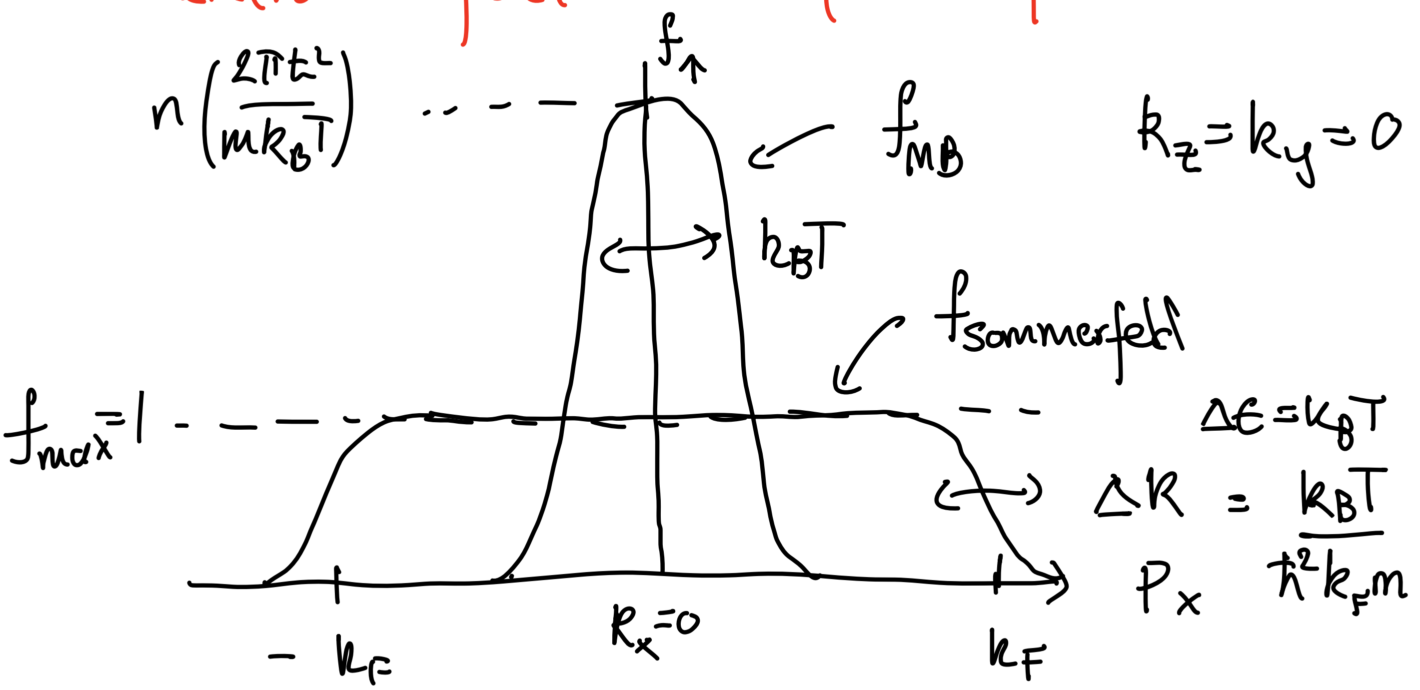
extracting a distribution function

think about 1 species of spin

$$\therefore \; f_{\text{sommerfeld}} = f_{FD}\left(\beta(\epsilon_p - \mu)\right) \le \underbrace{f_{max} = 1}_{\text{maximum possibl phase space density}}$$

Phase space vol per e^- $> (2\pi)^d$

extra factor 2 from spin



→ remember integral of f is # electrons

→ in MB there is no restriction on phase space density — if you add more electrons the dist just gets higher
→ scales vertically

→ in Sommerfeld theory it cannot get higher — it gets wider

→ however only a tiny fraction of the electrons are close enough to the FS to find an empty state via thermal excitation

But wait

How do we define $f(r, k)$ in QM given that $\Delta r \Delta k \gtrsim 1$ (Heisenberg)

- $k \leftrightarrow r$ conjugate $\vec{k} = -i\vec{\nabla}_r$

  $\vec{k}$ states $\longrightarrow \Delta \vec{r} = \infty$

  $\vec{r}$ states $\longrightarrow \Delta \vec{k} = \infty$

- In general we can use other bases

  eg $\psi(r) = e^{i\vec{k}\cdot\vec{r}} e^{-\frac{|r-r_0|^2}{4\sigma^2}}$

  $\Delta r \sim \sigma \qquad \Delta k \sim \frac{1}{\sigma}$

- Minimum phase space volume for 1 state

$$1 = \frac{1}{(2\pi)^d}\int_{\Delta r^d} d^3r \int_{\Delta k^d} d^3r \, f(r, k) \leq \left(\frac{\Delta r \Delta k}{2\pi}\right)^d$$

- $f(r, k)$ cannot change over a volume associated to 1 state

$$(r, k) \rightarrow (r + \Delta r, k + \Delta k)$$

$$\Delta f = \nabla_r f \cdot \Delta r \ll 1$$

$$\nabla_k f \cdot \Delta k \ll 1$$

- Fermi surface gives a sharp feature in k-space

$$\nabla_k f \Big|_{FS} = \nabla_k \epsilon \frac{\partial f}{\partial \epsilon} = \frac{\hbar^2 k_F}{m} \frac{1}{k_B T}$$

$$\therefore \nabla_r f \ll \frac{1}{\Delta r} \lesssim \Delta k \ll \frac{1}{|\nabla_k f|} \sim \frac{k_B T}{\hbar v_F}$$

$\therefore$ f varies on a length scale

$\sim 10^4 \times$ lattice spacing

ξ_{th} = thermal coherence length

⟶ length scale on which quantum coherent effects decay

3.10 Thermoelectrics in the Sommerfeld model

- **How is Seebeck coeff resolved?**

recall

$$\begin{array}{r} \text{el. current} \rightarrow \\ \\ \text{heat current} \rightarrow \end{array} \begin{pmatrix} j \\ \\ j_q \end{pmatrix} = \begin{pmatrix} L_{11} & L_{12} \\ \\ L_{21} & L_{22} \end{pmatrix} \begin{pmatrix} \vec{\mathcal{E}} \\ \\ -\vec{\nabla} T \end{pmatrix} \begin{array}{l} \leftarrow \text{ECF} \\ \\ \leftarrow \text{thermal gradient} \end{array}$$

– for $\nabla T = 0$ (isothermal)

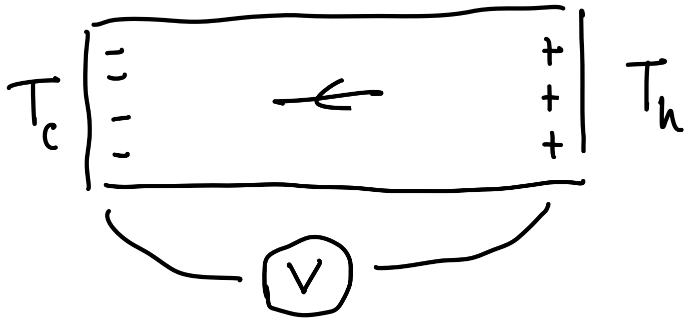
$$\vec{j} = L_{11} \vec{\mathcal{E}} \implies L_{11} = \sigma \quad \text{conductivity}$$

– for $\vec{j} = 0$ (open circuit)

$$\vec{\mathcal{E}} = \frac{L_{12}}{L_{11}} \vec{\nabla} T \implies \frac{L_{12}}{L_{11}} = S \quad \text{Seebeck}$$

$$\therefore L_{12} = S\sigma$$

Expt



Drude

$$\frac{S_{\text{theory}}}{S_{\text{expt}}} \simeq 10^3$$

Approach:

- Use same Boltzmann equation

$$\frac{\partial f}{\partial t} + \vec{v}(\vec{p})\cdot\nabla_r f + F(\vec{r})\cdot\nabla_{\vec{p}} f = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}$$

- Adapts directly to Sommerfeld

$$\vec{p} \to \hbar\vec{k}, \quad \vec{v} \to \frac{\hbar\vec{k}}{m}$$

in A&M convention is to us $\vec{k}$

$$f_{\text{eqm}} = \underbrace{\frac{2}{(2\pi)^3}}_{\substack{\text{states per unit volume} \\ \text{per unit } k\text{-space volume}}} f_{FD}(\beta(\epsilon_k - \mu))$$

Seebeck problem

- No EM potentials

$$F(r) = -e\vec{E} + \vec{v}\times\vec{B} = 0$$

- Thermal gradient

$$\therefore \quad T = T_0 + \delta T \qquad \vec{\nabla} T \parallel \vec{x} \quad (x \text{ direction})$$

$$\therefore \quad \mu = \mu + \delta\mu \qquad \delta\mu = \frac{\partial \mu}{\partial T}\bigg|\, \delta T \qquad (\text{fixed } n)$$

- Steady State

$$\therefore \quad \frac{\partial f}{\partial t} = 0$$

Simplifications

- Single scattering time approx

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = -\frac{1}{\tau}\left(f - f_0\right)$$

⟹ Combining

$$\boxed{\vec{v} \cdot \nabla_r f = -\frac{1}{\tau}\left(f - f_0\right)}$$

equation for f in a temperature gradient

- $\vec{r}$ - dependence only through T

$$\nabla_r f = \nabla_r T \left.\frac{df}{dT}\right|_n$$

- expand as $f = f_0 + \delta f$
- Solve for δf to linear order in δT

$$\delta f = - \tau \vec{v} \cdot \vec{\nabla}_r \delta T \left.\frac{df_0}{dT}\right|_n$$

- Calculate current density

$$\vec{j}_x = \frac{2}{(2\pi)^3}\int d^3k \, (-e\vec{v})\,(\overset{=0}{\cancel{f_0}} + \delta f) \qquad j_{eqm} = 0$$

$$= \tau e \left[\left.\frac{d}{dT}\right|_n \underbrace{\frac{2}{(2\pi)^3}\int d^3k \, \vec{v}\,\vec{v}^T f_0}_{u} \right] \vec{\nabla} T$$

use $\langle v_i v_j \rangle = \frac{1}{3}\delta_{ij}\langle v^2\rangle = \frac{2}{3m}\delta_{ij}\langle \epsilon_k \rangle$

$$= \frac{2\tau e}{3m} \left.\frac{du}{dT}\right|_n \vec{\nabla} T$$

$$= \underbrace{\frac{2\tau e}{3m} C_{el,vol}}_{-L_{12}} \vec{\nabla} T$$

$$S = \frac{L_{12}}{\frac{ne^2\tau}{m}} = -\frac{2}{3en} C_{el,vol}$$

$$\uparrow$$

$$C_{el,vol} \begin{cases} \frac{3}{2} k_B n & \text{(Drude)} \\ \frac{\pi^2}{2} k_B n \left(\frac{T}{T_F}\right) & \text{(Sommerfeld)} \end{cases}$$

$$\downarrow$$

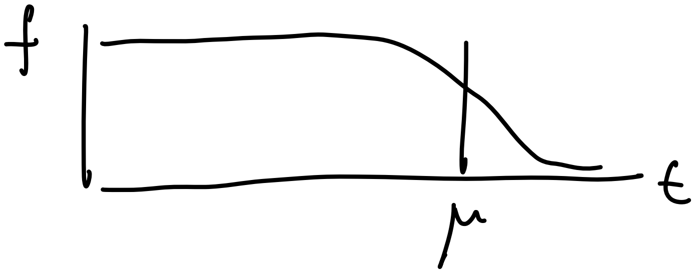
$$S = \begin{cases} -\frac{k_B}{e} \\ -\frac{\pi^2 k_B}{3e} \cdot \frac{T}{T_F} \end{cases}$$

But why - Structure of sommerfeld

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

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

$$c \equiv \frac{du}{dT} = \int d\epsilon \, g(\epsilon) \epsilon \frac{df}{dT}$$



$$f\left(\frac{\epsilon-\mu}{kT}\right)$$

$$\therefore \quad c = -\frac{1}{T} I_1 \qquad I_n = \int d\epsilon \, g(\epsilon) \epsilon (\epsilon-\mu)^n \frac{df}{d\epsilon}$$

$$\sigma \propto I_0 \qquad \sigma S = \frac{\sigma \Pi}{T} \propto I_1 \qquad \kappa \propto I_2$$

$$\frac{df}{d\epsilon} \rightarrow \text{even}$$

- **But wait**

– how can we have $f(r,k,t)$ in QM?

– $k \leftrightarrow r$ conjugate

$$\vec{k} = -i\vec{\nabla}_r$$ ← in precise terms

$\vec{k}$ state $\longrightarrow$ $\Delta r = \infty$

$\vec{r}$ state $\longrightarrow$ $\Delta k = \infty$

– however only need

$$\Delta k \, \Delta r \gtrsim \frac{1}{2}$$

– Pauli exclusion: Each state occupies Phase space vol $\sim 2\pi$

consider a single spin species for now

$$f \leq f_{max} = \frac{1}{(2\pi)^3}$$