Lecture 14

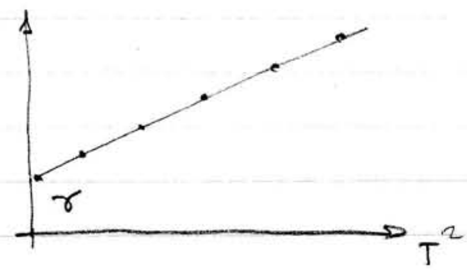
We saw that when $n \approx n_Q$ multiple occupancy of orbitals is possible and quantum statistics must be taken into account

"Degenerate Fermi gases" are ideal gases of fermions under those conditions (here, meaning of degenerate is different than usual meaning in QM where states have same energy)

Ex: conduction e^- in metals - outer e^- free from ions, conduct
white dwarf - atoms are ionized e^- in gas
neutron star - gas of neutrons
nuclear matter - gas of protons + neutrons
liquid ^3He - fermions too, but ideal gas approximation not valid

We'll treat conduction e^- in metals
Recall heat capacity in metals

$$C_V = \underbrace{\gamma T}_{e^-} + \underbrace{AT^3}_{\text{phonons}}$$



We'll be able to derive linear dependence of C_V on T

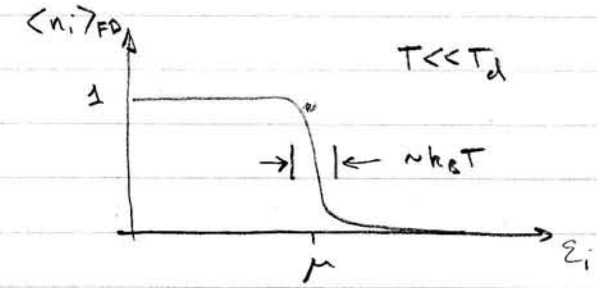
Recall $n_Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

Define degeneracy temperature T_d when $n = n_Q$:

$$T_d = \frac{h^2}{2\pi m k_B} n^{2/3}$$

when $T < T_d$ $\quad n > n_Q$
$\quad\quad\;\; T > T_d$ $\quad n < n_Q$

For typical metals $T_d \sim 50{,}000 - 100{,}000\,K$
so $n \gg n_Q$ at room $T = 300K$. Metals are <u>degenerate</u>



Occupancy $\langle n_i \rangle_{FD}$ is very close to a step function $(T=0)$
(We will use this to approximate solution)

Recall $N = \sum_i \langle n_i \rangle_{FD} = \sum_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}$ determines μ

Also $U = \sum_i \langle \varepsilon_i \rangle = \sum_i \langle n_i \rangle_{FD}\, \varepsilon_i = \sum_i \frac{\varepsilon_i}{e^{\beta(\varepsilon_i - \mu)} + 1}$

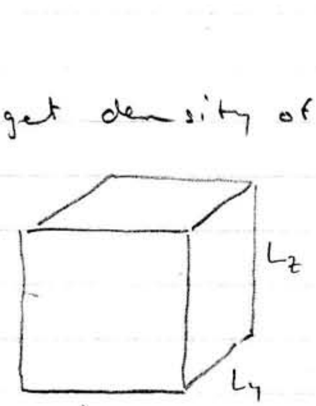
From that $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

At room $T = 300K$, can consider spectrum of orbitals to be continuous so $\sum \rightarrow \int$

$$\left.\begin{aligned} N &= \int_0^\infty d\varepsilon\; D(\varepsilon) \langle n(\varepsilon) \rangle \\ U &= \int_0^\infty d\varepsilon\; \varepsilon\, D(\varepsilon) \langle n(\varepsilon) \rangle \end{aligned}\right\}$$

$D(\varepsilon)$ = density of states
$D(\varepsilon)\,d\varepsilon$ = # of orbitals with energy between ε, $\varepsilon + d\varepsilon$

To get density of states, use same approach as before



e^- in box of volume $L_x L_y L_z = V$
e^- wavefunctions quantized
$k_x = \frac{n_x \pi}{L_x}$, $n_x = 1, 2, 3 \cdots$

same for y, z

so each state takes up volume in k-space $dk_x\, dk_y\, dk_z = \frac{\pi^3}{V}$

Energy of state $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$ with $k = \left(k_x^2 + k_y^2 + k_z^2\right)^{1/2}$

States with energy ε, $\varepsilon + d\varepsilon$ = # states in shell $\frac{4\pi}{8} k^2\, dk$

$$\therefore \; D(\varepsilon)\, d\varepsilon = \underset{\uparrow}{2} \cdot \frac{4\pi k^2\, dk}{8} \cdot \frac{V}{\pi^3} = \frac{V}{\pi^2} k^2\, dk$$

2 possible spins for e^- : $\uparrow$ or $\downarrow$

$$k = \left(\frac{2m\varepsilon}{\hbar^2}\right)^{1/2} \qquad dk = \left(\frac{2m}{\hbar^2}\right) \frac{d\varepsilon}{2\varepsilon^{1/2}}$$

$$\therefore \quad \boxed{D(\varepsilon)\, d\varepsilon = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}\, d\varepsilon}$$

So, we have

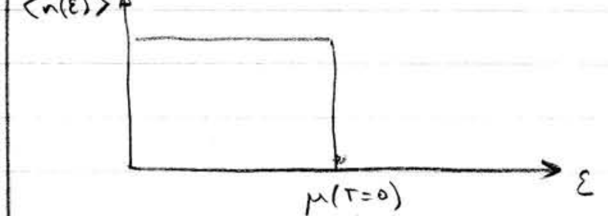
$$N = g_0 \int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{e^{\beta(\varepsilon-\mu)}+1} \qquad \text{Defined } g_0 \equiv \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}$$

$$U = g_0 \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}+1}$$

In general, we cannot solve these integrals analytically. However, at $T=0$ $\langle n(\varepsilon, T=0)\rangle$ is a step function, and integrals are trivial

Since at room T $\langle n(\varepsilon,T)\rangle$ is close to $\langle n(\varepsilon,0)\rangle$ we will expand about the $T=0$ solution to get an approximate answer. This is called the <u>Sommerfeld expansion</u>

First look at $T=0$.

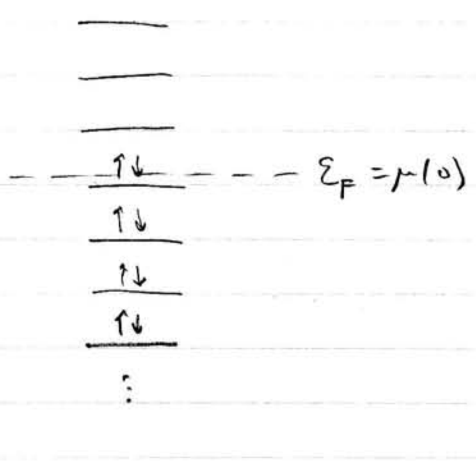


$$\langle n(\varepsilon,0)\rangle = 0 \quad \text{if } \varepsilon > \mu(0)$$
$$= 1 \quad \text{if } \varepsilon < \mu(0)$$

$$\therefore \quad N = \int_0^\infty \langle n(\varepsilon,0)\rangle\, D(\varepsilon)\, d\varepsilon = \int_0^{\mu(0)} D(\varepsilon)\, d\varepsilon$$
$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\mu(0)} \sqrt{\varepsilon}\, d\varepsilon = \frac{\cancel{2}}{3}\frac{V}{\cancel{2}\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu(0)^{3/2}$$

$$\boxed{\mu(0) = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3} \equiv \varepsilon_F}$$

Called the <u>Fermi Energy</u>



ε_F is the highest energy orbital occupied with e^-

Recall that e^- will fill up orbitals, at $T=0$ occupancy goes to 0 as soon as N e^- have been used up

Notice $\mu(0)$ depends on N, also V because that affects spacing between energy levels
$\mu(0) \sim n^{2/3}$ is <u>intensive</u>

Now $$U(0) = \int_0^\infty \langle n(\varepsilon,0)\rangle\, D(\varepsilon)\,\varepsilon\, d\varepsilon = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\varepsilon_F} \varepsilon^{3/2}\, d\varepsilon$$
$$= \frac{\cancel{2}}{5}\cdot\frac{V}{\cancel{2}\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon_F^{5/2} = \frac{3}{5}N\varepsilon_F$$

Compare to classical gas with MB statistics

$$U_{MB} = \frac{3}{2} N k_B T \quad , \qquad U_{FD} = \frac{3}{5} N \varepsilon_F$$

Even at $T=0$, $U_{FD} \gg 0$ because Pauli exclusion principle requires that e^- keep filling up energy levels

Define Fermi temperature $k_B T_F = \varepsilon_F$

(Almost the same as degeneracy temp T_d

$$k_B T_d = \frac{h^2}{2\pi m} n^{2/3} = 4\pi \frac{\hbar^2}{2m} n^{2/3} \sim (3\pi^2)^{2/3} \frac{\hbar^2}{2m} n^{2/3} = k_B T_F$$

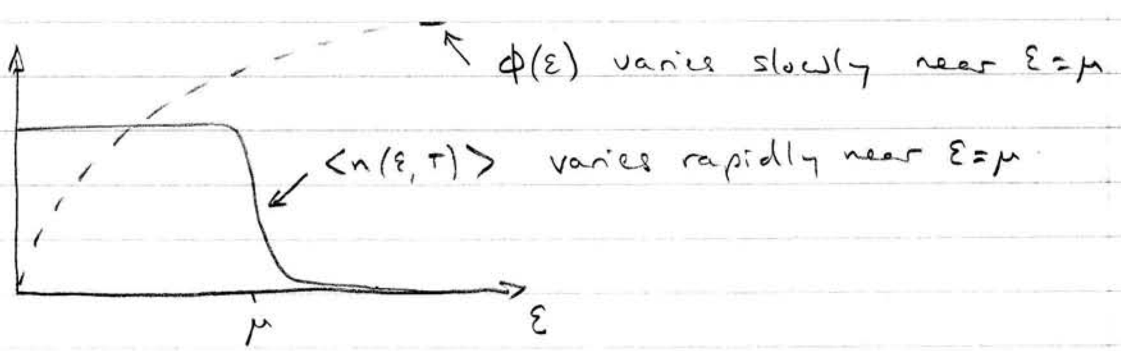
$T_F \sim 50{,}000 - 100{,}000\,K$ in metals)

Now consider $T > 0$. Since $\langle n(\varepsilon, T)\rangle$ is close to $\langle n(\varepsilon, 0)\rangle$ at room T, we'll use the <u>Sommerfeld expansion</u>

We're dealing with integrals of the form

$$I = \int_0^\infty d\varepsilon \, \langle n(\varepsilon,T)\rangle \, \varepsilon^n D(\varepsilon) \qquad \text{For } N,\ n=0\ ,\ U,\ n=1$$

Define $\phi(\varepsilon) \equiv \varepsilon^n D(\varepsilon)$



<u>Sommerfeld Expansion</u>

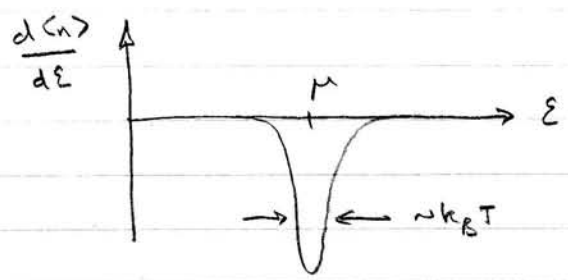
Define $\quad \Psi(\varepsilon) \equiv \int_0^{\varepsilon} \phi(\varepsilon')\, d\varepsilon'$

Integrate I by parts

$$I = \int_0^\infty \langle n(\varepsilon, T)\rangle \; \phi(\varepsilon)\, d\varepsilon$$

$$= \underbrace{\langle n(\varepsilon, T)\rangle}_{n(\infty, T) = 0} \underbrace{\Psi(\varepsilon)}_{\Psi(0) = 0} \Big|_0^\infty - \int_0^\infty d\varepsilon \; \Psi(\varepsilon) \; \frac{d\langle n(\varepsilon, T)\rangle}{d\varepsilon}$$

$$= -\int_0^\infty d\varepsilon \; \Psi(\varepsilon) \; \frac{d\langle n(\varepsilon, T)\rangle}{d\varepsilon}$$



$\frac{d\langle n\rangle}{d\varepsilon}$ is a very sharp function peaked at $\varepsilon = \mu$ width of $\sim k_B T$

$\Psi(\varepsilon)$ varies slowly near $\varepsilon = \mu$

$\therefore$ Expand $\Psi(\varepsilon)$ about $\varepsilon = \mu$

$$\Psi(\varepsilon) = \Psi(\mu) + \Psi'(\mu)\,(\varepsilon - \mu) + \frac{1}{2}\,\Psi''(\mu)\,(\varepsilon - \mu)^2 + \cdots$$

$$= \sum_{m=0}^{\infty} \frac{1}{m!}\, \Psi^{(m)}(\mu)\, (\varepsilon - \mu)^m$$

$$\therefore \quad I = -\sum_{m=0}^{\infty} \frac{1}{m!}\, \Psi^{(m)}(\mu) \int_0^\infty (\varepsilon - \mu)^m \; \frac{d\langle n(\varepsilon, T)\rangle}{d\varepsilon}\, d\varepsilon$$

$$\frac{d\langle n\rangle}{d\varepsilon} = \frac{-\beta e^{\beta(\varepsilon-\mu)}}{\left(e^{\beta(\varepsilon-\mu)}+1\right)^2}$$

$$\therefore \quad I = \sum_{m=0}^{\infty} \frac{1}{m!} \Phi^{(m)}(\mu) \underbrace{\int_0^{\infty} \frac{\beta e^{\beta(\varepsilon-\mu)}}{\left(e^{\beta(\varepsilon-\mu)}+1\right)^2} (\varepsilon-\mu)^m \, d\varepsilon}$$

Change variables to $x \equiv \beta(\varepsilon-\mu)$

$$= \beta^{-m} \int_{-\beta\mu}^{\infty} \frac{e^x}{(e^x+1)^2} x^m \, dx$$

Look at lower limit $\mu \sim \varepsilon_F$ so $\beta\mu = \mu/k_BT \gg 1$
Also integrand is negligible for $x < 0$, so its fine to replace lower limit with $-\infty$

So integral becomes $I_m = \int_{-\infty}^{\infty} \frac{e^x x^m}{(e^x+1)^2} \, dx$

Note that $\frac{e^x x^m}{(e^x+1)^2} = \frac{x^m}{(e^x+1)(1+e^{-x})}$ which is an odd function if m is odd

$\therefore \quad I_m = 0$ for m odd

For m even, we'll only need the two lowest order terms

$$I_0 = \int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2} \, dx = \left.\frac{-1}{e^x+1}\right|_{-\infty}^{\infty} = 1$$

$$I_2 = \int_{-\infty}^{\infty} \frac{e^x x^2}{(e^x+1)^2} \, dx = 2\zeta(2) = \frac{\pi^2}{3}$$

Riemann zeta function

(Deriving this takes a bit more algebra)

So: $\int_0^\infty \langle n(\varepsilon,T)\rangle\, \phi(\varepsilon)\, d\varepsilon = \sum_{\substack{m \\ \text{even}}} \frac{1}{m!} \Psi^{(m)}(\mu)\, (k_B T)^m\, I_m$

$$= \Psi(\mu) + (k_B T)^2 \frac{\pi^2}{6} \Psi''(\mu) + \cdots$$

Recall that $\Psi(\varepsilon) = \int_0^\varepsilon \phi(\varepsilon')\, d\varepsilon'$

$$\therefore \boxed{\int_0^\infty \langle n(\varepsilon,T)\rangle\, \phi(\varepsilon)\, d\varepsilon = \int_0^\mu \phi(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 \phi'(\mu) + \cdots}$$

the Sommerfeld expansion!

Now consider first integral

$$N = \int_0^\infty \langle n(\varepsilon,T)\rangle\, D(\varepsilon)\, d\varepsilon = \int_0^\mu D(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 D'(\mu) + \cdots$$

$$\cancel{N} \approx \underbrace{\int_0^{\varepsilon_F} D(\varepsilon)\, d\varepsilon}_{\substack{T=0 \text{ term} \\ = N}} + \underbrace{\int_{\varepsilon_F}^{\mu} D(\varepsilon)\, d\varepsilon}_{\approx D(\varepsilon_F)(\mu-\varepsilon_F)} + \frac{\pi^2}{6}(k_B T)^2 D'(\mu)$$

expect $\mu(T) \approx \varepsilon_F$

$$0 \approx D(\varepsilon_F)(\mu-\varepsilon_F) + \frac{\pi^2}{6}(k_B T)\, D'(\varepsilon_F)$$

Solve for $\mu(T)$:

$$\mu(T) \approx \varepsilon_F - \frac{\pi^2}{6}(k_B T)^2 \underbrace{\frac{D'(\varepsilon_F)}{D(\varepsilon_F)}}_{\frac{1}{2\varepsilon_F}} = \varepsilon_F - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right) k_B T$$

this is very small

So $\mu(T)$ decreases from $\mu(0) = \varepsilon_F$ as T increases