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 $\mu(T)$:

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

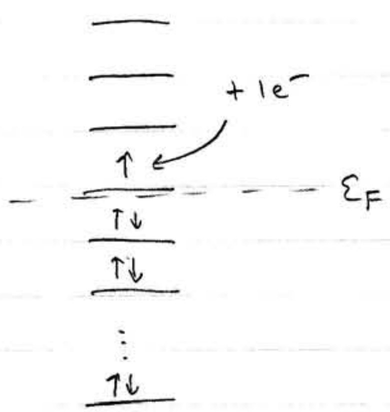
this is very small

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

Let's try to understand behavior of $\mu(T)$ better.
Recall that:

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{T,V} \qquad F \equiv U - TS$$

At $T \cong 0$

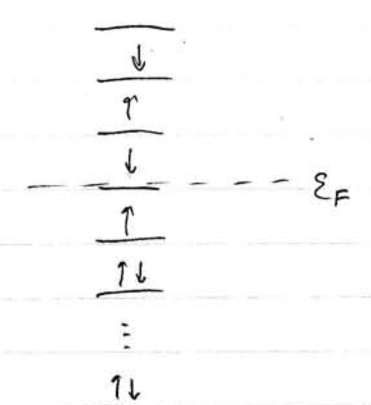


Gain in U from adding $1e^-$ is ε_F since that is the next level to fill

However $S=0$, and does not change. There is only 1 possible configuration since all the e^- occupy the lower levels

$$\therefore \quad \underset{\overset{\shortparallel}{1}}{\frac{\Delta F}{\Delta N}} = \Delta U - 0 = \varepsilon_F = \mu(0)$$

At $T > 0$



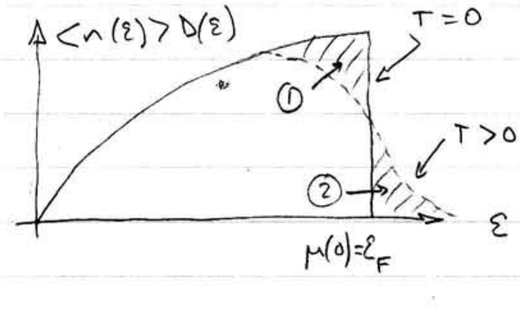
Now gain in U from adding $1e^-$ will on average still be $\sim \varepsilon_F$ (there are available levels higher and lower than ε_F)

But there is a gain in entropy because there are more levels that can be filled, hence more ways to fill them $\therefore \Delta S > 0$

so $\mu(T>0) \downarrow$ compared to $\mu(0)$

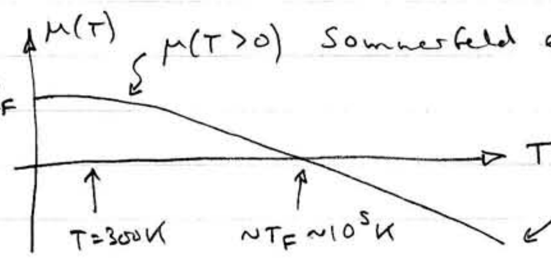
Another way to visualize this

$$N = \int_0^\infty \langle n(\varepsilon,T)\rangle D(\varepsilon)\, d\varepsilon$$ is true for all T



Area under curve must always be $= N$

Suppose $\mu(T>0) = \mu(0)$ (shown above) then the ~~are~~ area under that curve $= N$ too. However, area in ① < area in ② and area under putative $\langle n(\varepsilon,T>0)\rangle D(\varepsilon) > \langle n(\varepsilon,0)\rangle D(\varepsilon)$, which can't happen. The only way it can work is if $\underline{\mu(T>0) < \mu(0)}$



eventually get back <u>classical</u> $\mu(T) = \mu_{MB}$

Now calculate energy $U = \int_0^\infty \langle n(\varepsilon,T)\rangle \underbrace{\varepsilon D(\varepsilon)}_{\phi(\varepsilon)} d\varepsilon$

Using Sommerfeld expansion:

$$U(T) = \int_0^\mu \varepsilon D(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 \frac{d}{d\varepsilon}\left(\varepsilon D(\varepsilon)\right)\Big|_\mu$$

$$= \underbrace{\int_0^{\varepsilon_F} \varepsilon D(\varepsilon)\, d\varepsilon}_{U(0) = \frac{3}{5}N\varepsilon_F} + \underbrace{\int_{\varepsilon_F}^{\mu} \varepsilon D(\varepsilon)\, d\varepsilon}_{\approx (\mu-\varepsilon_F)\varepsilon_F D(\varepsilon_F)} + \frac{\pi^2}{6}(k_B T)^2 \underbrace{\left(D(\mu) + \mu D'(\mu)\right)}_{\approx D(\varepsilon_F) + \varepsilon_F D'(\varepsilon_F)}$$

since $\mu(T>0) \approx \varepsilon_F$ to lowest order

$D(\varepsilon) = g_0\, \varepsilon^{1/2} \qquad \therefore \quad D'(\varepsilon) = \dfrac{g_0}{2\varepsilon^{1/2}} = \dfrac{D(\varepsilon)}{2\varepsilon} \qquad g_0 = \dfrac{V}{2\pi^2}\left(\dfrac{2m}{\hbar^2}\right)^{3/2}$

Plugging in for μ in second term

$$U(T) = U(0) - \cancel{\frac{\pi^2}{12}\frac{(k_B T)^2}{\varepsilon_F}\varepsilon_F D(\varepsilon_F)} + \frac{\pi^2}{6}(k_B T)^2 D(\varepsilon_F) + \cancel{\frac{\pi^2}{6}(k_B T)^2 \varepsilon_F \cdot \frac{D(\varepsilon_F)}{2\varepsilon_F}}$$

$$= U(0) + \frac{\pi^2}{6}(k_B T)^2 D(\varepsilon_F)$$

Now can solve for $C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$

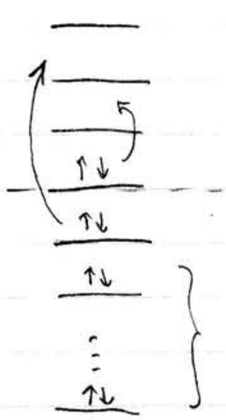
$$C_V = \frac{\pi^2}{3} k_B^2\, T\, D(\varepsilon_F) = \frac{\pi^2}{3} k_B^2\, T\, \underbrace{g_0}_{\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} = \frac{3}{2} N \varepsilon_F^{-3/2}} \varepsilon_F^{1/2}$$

$\therefore \boxed{C_V = \dfrac{\pi^2}{2} N k_B \dfrac{T}{T_F}}$ so we get linear dependence seen in experiments

For many metals (ex: alkali) $\gamma = \dfrac{\pi^2}{2} \dfrac{N k_B}{T_F}$ is accurate to ~ 20-30%

Compare to classical result $C_V = \frac{3}{2} N k_B$

For degenerate Fermi gas, <u>only</u> particles near ε_F can be promoted to higher states



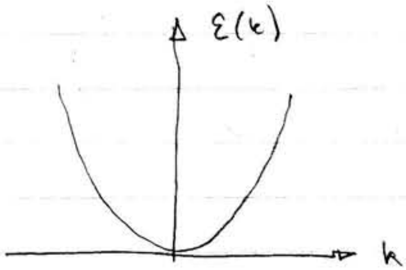
Only fraction $\sim N\dfrac{T}{T_F}$ contributes

$\therefore \; C_V \sim N k_B \dfrac{T}{T_F}$

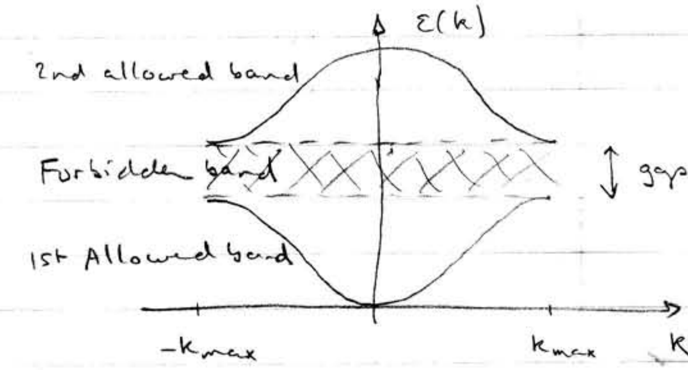
lower energy particles can't move up

Realistic materials

We assumed e^- in metal were "free" with energy $\mathcal{E}(k) = \frac{\hbar^2 k^2}{2m}$
When accounting for x-tal structure, e^- energy is more complicated:



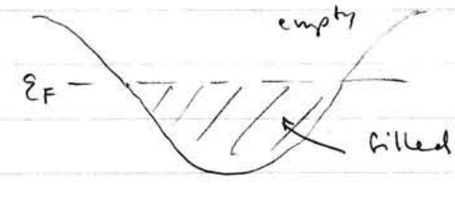
"free" e^-



e^- in x-tal

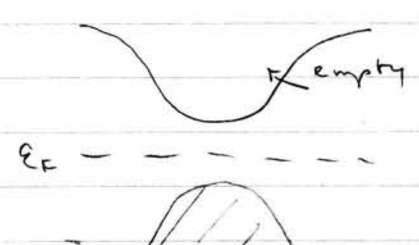
In real x-tal, there are allowed energy "bands" and forbidden "bands", that create energy gaps

For a metal – $\mathcal{E}_F$ is within one band



At $T > 0$, e^- near $\mathcal{E}_F$ can be excited. These contribute to conduction

For an insulator – $\mathcal{E}_F$ is in energy gap between two bands



Here, there are no empty states close to occupied states, e^- are "stuck" in place and cannot conduct electricity

In semiconductors, gap $\sim k_B T$ so a few e^- can jump across gap

Lecture 15

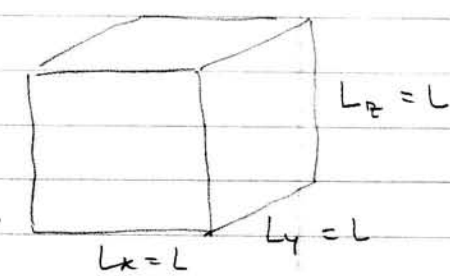
We'll consider a gas of bosons. Recall that bosons can occupy the same quantum state

$$\langle n(\varepsilon, T)\rangle_{BE} = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} \geq 0$$

$\therefore$ $\mu < \varepsilon$ for all orbitals, including ground state ε_0

Let's estimate ε_0, and μ

Consider a box of bosons (Ex: ^4He)



Again $\varepsilon(k) = \dfrac{\hbar^2 k^2}{2m}$

$$k = \sqrt{k_x^2 + k_y^2 + k_z^2} \qquad k_i = \frac{n_i \pi}{L} \quad n_i = 1, 2 \cdots$$

For simplicity $L_x = L_y = L_z$

$\therefore$ Ground state ε_0 is

$$\varepsilon_0 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (1^2 + 1^2 + 1^2) \qquad n_x = n_y = n_z = 1$$

For m = mass of ^4He, $L = 1\,cm$
$= 6.6 \times 10^{-27}\,kg$

$$\varepsilon_0 \sim 10^{-37}\,J \sim 5 \times 10^{-19}\,eV \qquad \varepsilon_0/k_B \sim 10^{-14}\,K$$

Practically zero!

Now consider what μ must be as $T \to 0$

As $T \to 0$ we expect all the bosons to occupy the ground state
If $N \sim 10^{22}$ and

$$N = \frac{1}{e^{\beta(\varepsilon_0 - \mu)} - 1} \gg 1$$

$\therefore$ Denominator must be very small $\Rightarrow$ i.e. $\beta(\varepsilon_0 - \mu)$ must be very small

As $T \to 0$ $\quad N \approx \frac{1}{\cancel{1} + \beta(\varepsilon_0 - \mu) \cancel{-1}} = \frac{k_B T}{\varepsilon_0 - \mu}$

$$\therefore \mu(T \to 0) \approx \varepsilon_0 - \frac{k_B T}{N}$$

so μ is less than ε_0 (as expected) but extremely close to ε_0 for sufficient small T and for $N \gg 1$

How small must T be for the ground state occupancy to be large? We'll figure this out soon.

First, let's compare how close $\mu(T \to 0)$ is to the first excited state:

$$\varepsilon_1 = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 (2^2 + 1^2 + 1^2) = \varepsilon_0 + \Delta\varepsilon$$

$$\Delta\varepsilon = 3 \cdot \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 = 2.5 \times 10^{-37} \text{ J} \sim 10^{-19} \text{ eV}$$

Again, tiny

On the other hand, for a small $T = 1\text{mK}$

$$\mu(T) = \varepsilon_0 - 1.4 \times 10^{-48} \text{ J} = \varepsilon_0 - 10^{-30} \text{ eV}$$

even tinier!

So, μ is closer to ε_0 than ε_1 is by orders of magnitude

This means that
$e^{\beta(\varepsilon_0-\mu)}$ is much closer to 1 than $e^{\beta(\varepsilon_1-\mu)}$

What are the consequences of this?
Compare the occupancies of ground state vs. excited state at $T = 1\,mK$

If bosons obeyed MB statistics, we would expect

$$\frac{\langle n(\varepsilon_1,T)\rangle_{MB}}{\langle n(\varepsilon_0,T)\rangle_{MB}} = \frac{e^{-\beta(\varepsilon_1-\mu)}}{e^{-\beta(\varepsilon_0-\mu)}} = e^{-\beta\Delta\varepsilon} = e^{-1.8\times10^{-11}}$$

$$\approx 1 - 1.8\times10^{-11} = 1$$

Basically no difference. Makes sense, spacing between levels $\Delta\varepsilon = \varepsilon_1 - \varepsilon_0 \lll k_B T$ ($\sim 10^{-14}\,K$ vs. $10^{-3}\,K$)

Now, use <u>correct</u> BE statistics:

$$\langle n(\varepsilon_0,T)\rangle_{BE} = N = 10^{22}$$

$$\langle n(\varepsilon_1,T)\rangle_{BE} = \frac{1}{e^{\beta(\varepsilon_1-\mu)}-1} \approx \frac{1}{e^{\beta\Delta\varepsilon}-1}$$

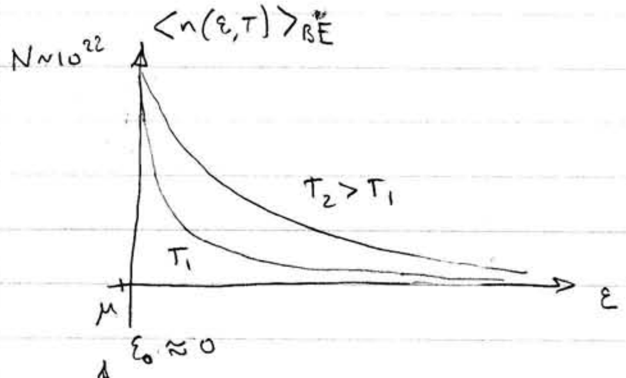
$$\varepsilon_1 - \mu = \varepsilon_1 - \varepsilon_0 + \frac{kT}{N} \approx \Delta\varepsilon$$

$$\approx \frac{1}{1.8\times10^{-11}} \approx 5\times10^{10}$$

$$\therefore \frac{\langle n(\varepsilon_1,T)\rangle_{BE}}{\langle n(\varepsilon_0,T)\rangle_{BE}} \approx 5\times10^{-12} \quad !!$$

Big difference

BE distribution is strange; it favors putting the great majority of the particles in the ground state at a sufficiently low temperature, much more than that expected from MB statistics.



This is called Bose-Einstein condensation

slightly offset μ for low T ensures that $\langle n(\varepsilon,T)\rangle_{BE}$ doesn't blow up when $\varepsilon = \varepsilon_0$

Next step is figuring out temperature at which this starts to happen.

Total # of particles:

all excited states $i>0$

$$N = \sum_i \langle n(\varepsilon_i,T)\rangle_{BE} = N_0 + N_e$$

treat ground state seperately

Spacing between levels is still very small, so we can write

$$N_e = \int_0^\infty D(\varepsilon)\,\langle n(\varepsilon,T)\rangle_{BE}\,d\varepsilon$$

technically should be ε_1, but $\varepsilon_1 \approx 0$