

Lecture # 8

From Drude to Sommerfeld.
CLASSICAL SEMI-QUANTUM

Q. Why Drude model was not accounting for the specific heat of a metal (recall the prediction was $\sim \frac{3}{2} k_B T$)?

A: B/c one needs to use quantum mechanics, i.e. instead of Boltzmann-Maxwell distribution go for Fermi-Dirac:

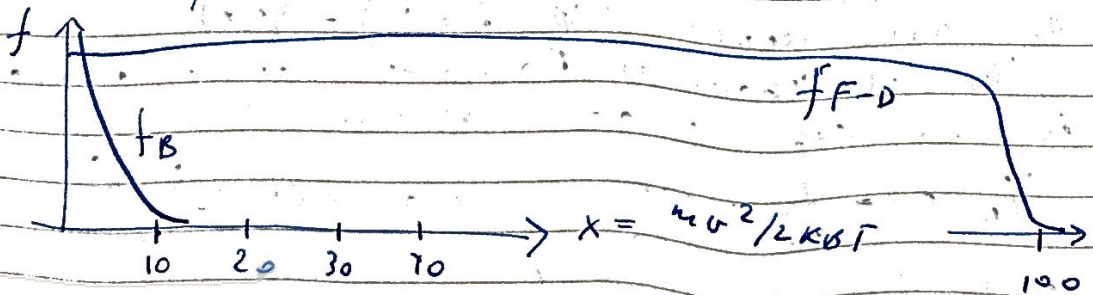
$$f_B(v) = \frac{N}{V} \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T}$$

vs.

$$f_{F-D}(v) = \frac{(m/h)^3}{4\pi^2} \frac{1}{e^{[mv^2/2 - k_B T_0]} + 1} \cdot \frac{N}{V} = \int f(v) dv$$

calculate. to get T_0

For any relevant temperatures $\leq 10^3$ K the difference is HUGE!



* Sommerfeld model is "Drude model" where we replace f_B by f_{F-D} .

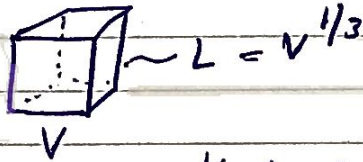
Property of the electron gas: at $T=0$.

Solving a problem of N electrons at the ground state when those N electrons are fermions (i.e. the Pauli exclusion principle in action)

We start by writing down the Sch. equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(r) = \epsilon \psi(r)$$

To solve the equation we need to assume some kind of boundary condition. In our case let's take it to be a macroscopically large cube



We can assume that $\psi(r)|_{r=\text{surface}} = 0 \Rightarrow$ standing waves, which are stationary states not

describing the transfer of energy or heat or electricity. So we can ignore the surface all together!

electron starts here reenters the "surface" from other side $\Big| =$ the periodic boundary conditions

That's why the electronic "band" structure is calculated on a torus manifold for 3D.

Q. Can we calculate electronic structure of a solid on a Mobius strip?

All this means: $\psi(\vec{r} + \vec{L}) = \psi(\vec{r})$

this is known as Born-von Karman boundary cond. in this case a good solution is:

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} \quad \text{and} \quad \epsilon(\vec{k}) = \frac{\hbar^2 |\vec{k}|^2}{2m}$$

$$\text{and} \int d\vec{r} |\psi(\vec{r})|^2 = 1$$

Q: Why \vec{k} -vector is important?

A: $\psi_{\vec{k}}(\vec{r})$ is the eigenstate of $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial \vec{r}} = \frac{\hbar}{i} \nabla$

$$\begin{aligned} \text{check thus } \frac{\hbar}{i} \frac{\partial}{\partial \vec{r}} \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}} &= \frac{\hbar}{i} \frac{1}{\sqrt{V}} i\vec{k} e^{i\vec{k} \cdot \vec{r}} \\ &= \frac{\hbar \vec{k}}{1} \psi_{\vec{k}}(\vec{r}) \quad \text{so } \hat{p} \psi_{\vec{k}}(\vec{r}) = \frac{\hbar \vec{k}}{1} \psi_{\vec{k}}(\vec{r}) \end{aligned}$$

so $\hbar \vec{k}$ is the eigenstate of the \hat{p} operator.

$$\bar{p} = \hbar \bar{k} \quad v = \frac{p}{m} = \frac{\hbar}{m} k \quad ; \quad \epsilon = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

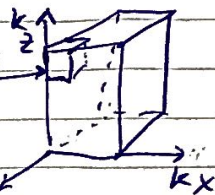
If \bar{k} is a wave vector the $e^{i\bar{k}\cdot\bar{r}} = \text{const}$ for any plane \perp to \bar{k} since the plane is defined by $\bar{k}\cdot\bar{r} = \text{const}$ and periodic along \bar{k} with $\lambda = 2\pi/\bar{k}$.

From the boundary condition $\psi(\bar{r}+L) = \psi(\bar{r})$,

$$e^{i\bar{k}(\bar{r}+L)} = e^{i\bar{k}\bar{r}} \Rightarrow e^{i\bar{k}L} = 1 \Rightarrow k = \frac{2\pi}{L} \cdot n$$

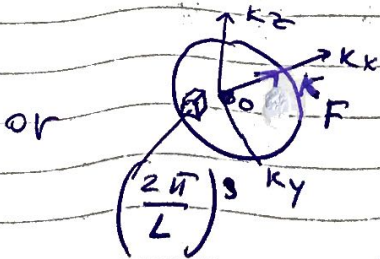
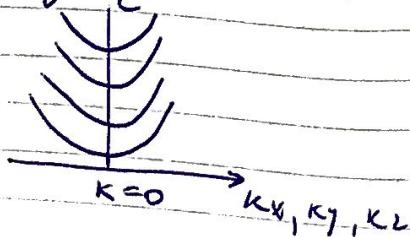
So in k -space the allowed k values are:

$$k_x, k_y, k_z \text{ with absolute minimum } k_x \cdot k_y \cdot k_z = \left(\frac{2\pi}{L}\right)^3$$



So the region Ω in k -space will contain $\frac{\Omega}{(2\pi/L)^3}$ available k points or k -values.

Now we will build up the ground state of N electrons by placing those into those cells - 2 per point. The one electron states are defined by \bar{k} and projection of spin $\pm \hbar/2$.



the radius $k_F = ?$

$$\left(\frac{2\pi k_F}{3}\right)^3 \cdot \left(\frac{V}{8\pi^3}\right)$$

the number of available k values $= \frac{k_F^3}{6\pi^2} \cdot V$

So in each k point we can place 2 electrons

$$N = 2 \frac{k_F^3}{6\pi^2} \cdot V = \frac{k_F^3}{3\pi^2} V \Rightarrow \boxed{n = \frac{k_F^3}{3\pi^2}}$$

The momentum of the highest state

$$\hbar k_F = p_F = \text{the Fermi momentum}$$

$$\epsilon_F = \frac{p_F^2}{2m} = \text{the F. energy}$$

$$v_F = \frac{p_F}{m} = \text{the F. velocity}$$

v_F is analogous to $v = \left(\frac{3k_B T}{m}\right)^{1/2}$ for gases.

It is convenient to re-express these in terms of n or $r_s/a_0 \approx 2-4$ for most metals.

e.g. $\frac{1}{n} = \frac{4\pi r_s^3}{3}$ or $r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$

so $k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{1.92}{r_s} \approx \frac{2}{r_s}$ or

$$k_F = \frac{3.63}{r_s/a_0} \text{ \AA}^{-1}$$

Since $k_F \sim \text{few \AA}^{-1}$
 $\lambda = \frac{2\pi}{k_F} \sim \text{few \AA}$

$$v_F = \left(\frac{\hbar}{m}\right) k_F = \frac{4.2}{r_s/a_0} \cdot 10^8 \text{ cm/sec} \sim 1\% \text{ of } c$$

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{e^2}{2a_0}\right) (k_F a_0)^2 \quad (a_0 = \frac{\hbar^2}{m e^2})$$

$$\frac{e^2}{2a_0} = \text{Rydberg (Ry)} = 13.6 \text{ eV} \quad \text{the ground state of H atom}$$

$$\epsilon_F = \frac{50.1 \text{ eV}}{(r_s/a_0)^2} \approx \frac{50.1}{(2-4)^2} \approx 3-12 \text{ eV}$$

The total energy of the N free electrons:

$$E = 2 \sum_{k < k_F} \frac{\hbar^2 k^2}{2m}$$

In general we can write down for a smooth function

$$\sum_k F(k) = \frac{V}{8\pi^3} \int F(\vec{k}) d\vec{k} \rightarrow \frac{1}{8\pi^3} \int d\vec{k} F(\vec{k})$$

Volume of a smallest box $\Delta \vec{k}$

L8

Energy per unit volume: $\frac{E}{V} = \frac{1}{4\pi^3} \int_{0 \leq k_x, k_y, k_z \leq k_F} d\vec{k} \frac{\hbar^2 k^2}{2m} =$
 $= \frac{1}{4\pi^3} \int_0^{k_F} \frac{4\pi k^2 \hbar^2 k^2}{2m} dk = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m}$

$\frac{\bar{E}}{N} = \frac{E}{N/V} \cdot \frac{1}{V} = \frac{E}{V} \cdot \frac{3\pi^2}{k_F^3} = \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m} \cdot \frac{3\pi^2}{k_F^3} = \frac{3}{5} \epsilon_F$
 $\frac{N}{V} = \frac{k_F^3}{3\pi^2}$

We can now introduce the Fermi temperature:

$$T_F = \frac{\epsilon_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \cdot 10^4 \text{ K}$$

Notice for a classical gas $\frac{3}{2} k_B T \rightarrow 0$ if $T \rightarrow 0$
But not in our ^{quantum} case!

Since we have the total energy of the system calculate compressibility: the ground state pressure per electron:

$P = -\frac{\partial E}{\partial V} / N$ $\frac{E}{N} = \frac{3}{5} \epsilon_F = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} = \frac{3}{5} \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3} \sim \hbar^{2/3} = N^{2/3}$
 so $-\frac{\partial E}{\partial V} / N = \frac{2}{3} \frac{E}{V}$

Compressibility κ or bulk modulus $B = \frac{1}{\kappa} = -V \frac{\partial P}{\partial V}$

Since $E \sim V^{-2/3} \Rightarrow P \sim V^{2/3} / V = V^{-5/3}$ so
 $B = -V \frac{\partial P}{\partial V} \sim -V (-5/3) V^{-5/3-1} \sim \frac{5}{3} V^{-5/3} = \frac{5}{3} P$
 $= \frac{5}{3} \cdot \frac{2}{3} \frac{E}{V} = \frac{10}{9} \frac{E}{V} = \frac{2}{3} \hbar \epsilon_F$ or
 $B = \left(\frac{6.13}{r_s/a_0} \right)^5 \cdot 10^{10} \text{ Dynes/cm}^2$

OK THIS IS ALL ABOUT THE GROUND STATE OR $T=0$, WHAT ABOUT FINITE T?

The main way to introduce T into our formulae is to recall we are not dealing with a gas of bosons but rather FERMIONS so the probability of a one-electron level to be occupied at temp. T for N electron system is

$$f^N = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}$$

Let's try to calculate electronic contribution to the specific heat

$$C_V = \frac{1}{V} \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V \quad \text{where } U = \overset{\substack{\uparrow \\ \text{internal} \\ \text{energy}}}{U}$$

The internal energy

$$U = \int \frac{d^3k}{(2\pi)^3} \epsilon(\mathbf{k}) f(\epsilon(\mathbf{k})) \quad \text{where}$$

$$f(\epsilon(\mathbf{k})) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$

$$\text{also } n = \int \frac{d^3k}{(2\pi)^3} f(\epsilon(\mathbf{k}))$$

How to evaluate these integrals?

$$\begin{aligned} \int \frac{d^3k}{(2\pi)^3} F(\epsilon(\mathbf{k})) &= \frac{1}{(2\pi)^3} \int 4\pi k^2 dk F(\epsilon(\mathbf{k})) = \int_0^{\infty} \frac{k^2 dk}{\pi^2} F(\epsilon) \\ &= \int_{-\infty}^{\infty} d\epsilon g(\epsilon) F(\epsilon) \end{aligned} \quad \begin{aligned} \uparrow \\ \epsilon = \frac{\hbar^2 k^2}{2m} \end{aligned}$$

$$\text{where } g(\epsilon) = \begin{cases} \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\epsilon}{\hbar^2}} & \epsilon > 0 \\ 0 & \epsilon < 0 \end{cases}$$

$g(\epsilon)$ the number of 1-electron states between ϵ and $\epsilon + d\epsilon$ divided by V also known as the density of states per volume.

$$g(\epsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\epsilon}{\hbar^2}}$$

$$= \frac{3}{2} \frac{n}{\epsilon_F} \left(\frac{\epsilon}{\epsilon_F} \right)^{1/2}$$

recall $n = \frac{k_F^3}{3\pi^2}$

and $\epsilon_F = \frac{\hbar^2 k_F^2}{2m} \Rightarrow$

$k_F = \left(\frac{2m\epsilon_F}{\hbar^2} \right)^{1/2}$

and then the density of states at the Fermi level:

$$g(\epsilon_F) = \frac{3}{2} \frac{n}{\epsilon_F} = \frac{m k_F}{\hbar^2 \pi^2}$$

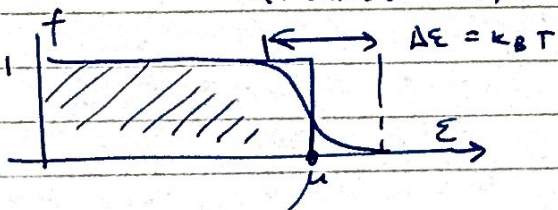
; so how we can rewrite

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

$$\left\{ \begin{aligned} U &= \int_{-\infty}^{\infty} d\epsilon g(\epsilon) \epsilon f(\epsilon) \\ n &= \int_{-\infty}^{\infty} d\epsilon g(\epsilon) f(\epsilon) \end{aligned} \right.$$

How to evaluate these integrals?

① Notice that $T=0$ and $T \neq 0$ differs only a bit around ϵ_F i.e.



so $\int_{-\infty}^{\infty} d\epsilon \dots \approx \int_{-\infty}^{\epsilon_F} d\epsilon + \text{little extra}$
of how the function behaves at μ .

$$\int_{-\infty}^{\epsilon_F} H(\epsilon) f(\epsilon) d(\epsilon)$$

if H is smooth, we can use the Taylor expansion.

$$H(\epsilon) = \sum_{n=0}^{\infty} \frac{d^n H(\epsilon)}{d\epsilon^n} \bigg|_{\epsilon=\mu} \times \frac{(\epsilon - \mu)^n}{n!}$$

as the result +

$$\int_{-\infty}^{\infty} H(\epsilon) f(\epsilon) d\epsilon = \int_{-\infty}^{\mu} H(\epsilon) d\epsilon + \sum_{n=1}^{\infty} (k_B T)^{2n} \text{an} \frac{d^{2n-1} H(\epsilon)}{d\epsilon^{2n-1}} \bigg|_{\epsilon=\mu} + O\left(\frac{k_B T}{\mu}\right)$$

See Appendix C in AEM

So finally: the SOMMERFELD EXPANSION.

$$\int_{-\infty}^{\infty} f(\epsilon) g(\epsilon) d\epsilon = \int_{-\infty}^{\mu} f(\epsilon) g(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 f'(\mu) g(\mu) + \frac{7\pi^4}{360} (k_B T)^4 f'''(\mu) g(\mu) + O\left(\frac{(k_B T)^6}{\mu^2}\right)$$

First calculate $\mu(T)$ See page

Let's illustrate how to use this SOMMERFELD expansion

$$U = \int_0^{\infty} \underbrace{f(\epsilon) g(\epsilon)}_{f(\epsilon) g(\epsilon)} \epsilon d\epsilon$$

$$U = \int_0^{\mu(T)} \epsilon g(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 \frac{d}{d\epsilon} [\epsilon g(\epsilon)]_{\epsilon=\mu} + \dots$$

Let's split this integral:

$$\int_0^{\mu(T)} \epsilon g(\epsilon) d\epsilon = \int_0^{\mu(0)} \dots + \int_{\mu(0)}^{\mu(T)} \dots$$

Total energy E for $T=0!$

we already calculated this so

recall $\frac{g(\epsilon)}{V} = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}$

$$\frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^{\mu(0)} \epsilon^{3/2} d\epsilon =$$

$$= \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{2}{5} [\mu(0)]^{5/2} = \frac{3}{5} \mu(0) \frac{1}{3\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2}$$

$$\bullet \mu(0)^{3/2} = \frac{3}{5} \mu(0) \cdot g(\mu(0))$$

Since the shift in the chemical potential is small the second integral:

$$\approx \mu(0) g(\mu(0)) [\mu(T) - \mu(0)] = \dots$$

Let's plug in our formula for $\mu(T)$ from page 9.

$$n = \int_0^{\infty} \underbrace{g(\epsilon)}_{=g(\epsilon)} f(\epsilon) d\epsilon \approx \int_0^{\mu(T)} g(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 \cdot \frac{dg}{d\epsilon} \Big|_{\mu}$$

$$\begin{aligned} \int_0^{\mu(T)} g(\epsilon) d\epsilon &= \int_0^{\mu(0)} g(\epsilon) d\epsilon + \int_{\mu(0)}^{\mu(T)} g(\epsilon) d\epsilon = \\ &= \cancel{n} + \int_{\mu(0)}^{\mu(T)} g(\epsilon) d\epsilon = \\ &= n + g(\mu(0)) (\mu(T) - \mu(0)) \end{aligned}$$

$$\begin{aligned} n &= n + g(\mu(0)) (\mu(T) - \mu(0)) + \frac{\pi^2}{6} (k_B T)^2 \cdot \frac{dg}{d\epsilon} \Big|_{\mu} \\ \Rightarrow \mu(T) &= \mu(0) - \frac{\pi^2}{6} (k_B T)^2 \frac{g'(\mu)}{g(\mu)} \end{aligned}$$

for free electrons

$$g(\epsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2m\epsilon}{\hbar^2}} \quad \text{or } \sim \sqrt{\epsilon} \quad \text{so } (\sqrt{\epsilon})' = \frac{1}{2\sqrt{\epsilon}}$$

we get

$$\begin{aligned} \mu(T) &= \mu(T=0) \left[1 - \frac{\pi^2}{6} (k_B T)^2 \frac{1}{2\sqrt{\epsilon}} \frac{1}{\sqrt{\epsilon}} \right] \\ &= \mu(T=0) \left[1 - \frac{\pi^2}{12} (k_B T)^2 \frac{1}{\mu^2(0)} \right] = \\ \boxed{\mu(T) &= \mu(0) \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\mu(0)} \right)^2 \right]} \end{aligned}$$

This is very interesting since it shows that as we raise T our chem. potential or the Fermi level will go up and some bands start being seen in the spectra. So don't be surprised if your ARPES data move with T !

back to the internal energy U :

for the ~~the~~ integral $\mu(0) g(\mu(0)) [\mu(T) - \mu(0)] =$

$$= -g(\mu(0)) \frac{\pi^2}{12} (k_B T)^2$$

here I used the fact that

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

and since $g(\epsilon) \sim \epsilon^{1/2}$

the second term is $\frac{d}{d\epsilon} (\epsilon g(\epsilon)) = \frac{3}{2} g(\epsilon)$ and hence

$$\frac{\pi^2}{4} \cdot (k_B T)^2 \cdot g(\mu(0))$$

Combining all the results we get

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

Now we can immediately get c_v :

$$c_v = \left(\frac{\partial U}{\partial T} \right)_N = \frac{\pi^2}{3} k_B^2 T g(\mu(0)) \quad \text{or with } g(\epsilon_F) = \frac{3}{2} \frac{n}{\epsilon_F}$$

$$c_v = \frac{\pi^2}{2} \left(\frac{k_B T}{\epsilon_F} \right) n k_B$$

$$c_v \sim T !!!$$

Compare to the ideal gas $c_v = \frac{3}{2} k_B n$
~~suppress~~ reduces this value by

$$\left(\frac{k_B T}{\epsilon_F} \right) \frac{\pi^2}{3} \sim 10^{-2}$$

so electrons PRACTICALLY DO NOT CONTRIBUTE
 TO THE SPECIFIC HEAT!

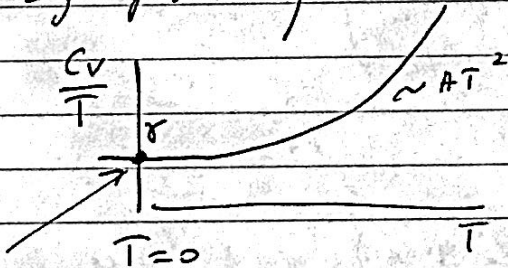
So realistically

$$C_V = \gamma T + AT^3$$

\uparrow electrons \uparrow ions

or $\frac{C_V}{T} = \gamma + AT^2$

so we can get the electron contribution by plotting



Contribution from free electrons.