Lecture 8
Free Electrons

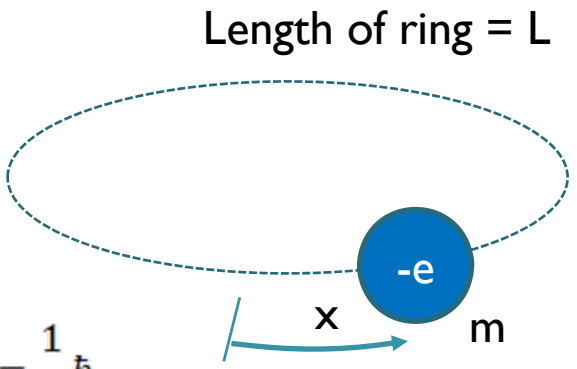
"Free electron" is like free lunch

Born – von Karman on Electrons

- One Dimension

$$\psi(x) = \psi(x + L)$$ Born – von Karman boundary condition

$$\psi(x) = \frac{1}{\sqrt{L}} e^{ikx}, \quad k = \frac{2\pi n}{L}, \qquad n = \text{integer}$$



Quantum Numbers $\quad p = \hbar k, \qquad \varepsilon = \frac{\hbar^2 k^2}{2m}, \quad S_z = \frac{1}{2}\hbar$

- D - Dimensions

Generalize ring to a torus (2d), a cube with periodic boundary (3d) etc.
Define D as spatial dimension.

$$\psi(\boldsymbol{x}) = \psi(\boldsymbol{x} + \boldsymbol{L}) \qquad \boldsymbol{L} = (L, L, \ldots, L) \quad D - vector$$

$$\psi(\boldsymbol{x}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{x}}, \qquad k_i = \frac{2\pi n_i}{L}, \quad i = 1..D, \qquad n_i = \text{integer}, \qquad V = L^D$$

Quantum Numbers $\quad \boldsymbol{p} = \hbar\boldsymbol{k}, \qquad \varepsilon = \frac{\hbar^2 k^2}{2m}, \quad S_z = \frac{1}{2}\hbar$

Will consider only D=3, from now on in this note.

Free electrons: Fermi Sea at T=0

DOS $$dN = 2\frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} = V\frac{k^2 dk}{\pi^2} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon}\,d\varepsilon = g(\varepsilon)d\varepsilon$$

$$g(\varepsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sqrt{\varepsilon} \propto \sqrt{\varepsilon}$$ in 3d

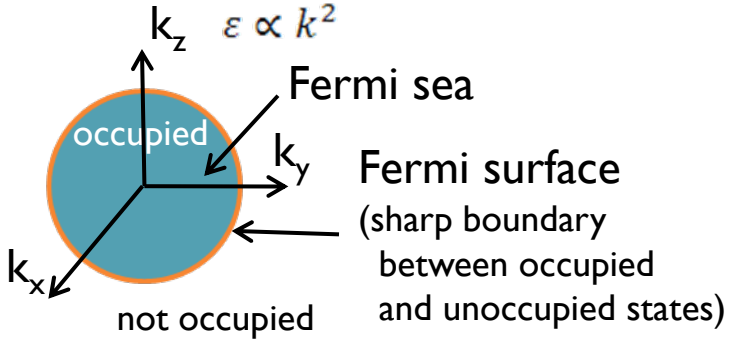
Fermi-Dirac Statistics and Number of particle numbers

give the energy cutoff (μ(T=0)): $$N = \int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon_F}{\hbar^2}\right)^{\frac{3}{2}}$$

Fermi energy $$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \equiv \frac{\hbar^2 {k_F}^2}{2m}$$

Fermi momentum $$k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}$$

Fermi temperature $$T_F \equiv \frac{\varepsilon_F}{k_B}$$



Questions

For the most part, the electrons in Cu are described well as "free electrons." Cu forms an fcc crystal with a = 3.61 Å. Assuming that one free electron is contributed per Cu, estimate the following quantities.

- Fermi energy (eV)
- Fermi temperature (K)
- Fermi momentum ($Å^{-1}$)
- r_s
- Fermi velocity (c)

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}}$$

$$r_s = \left(\frac{3V}{4\pi N}\right)^{\frac{1}{3}}, \qquad \frac{4\pi r_s^3}{3} = \frac{V}{N}$$

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Size of "room" for each electron
~ inter-electron distance
Characterizes electron density

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}} = \left(\frac{9\pi}{4}\right)^{\frac{1}{3}} \frac{1}{r_s} = \frac{1.92}{r_s}$$

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{(\hbar c)^2}{2mc^2} k_F^2 \sim \frac{(2000\ eV\text{Å})^2}{1e6\ eV} k_F^2 \sim 4k_F^2\ (= 3.8\ k_F^2\ ) \qquad \text{if } k_F \text{ in Å}^{-1} \text{ and } \varepsilon_F \text{ in eV}$$

Numbers, numbers … for typical metals (Au, Cu, Al, Na …)

$r_s = 1 \sim 2$ Å

$r_s \sim a \sim \frac{1}{k_F}$

$k_F = 1 \sim 2$ Å^{-1}

$$v_F \sim \frac{\hbar k_F}{m} = \frac{\hbar c\ c}{mc^2} k_F \sim \frac{2000\ eV\text{Å}}{0.5e6\ eV} \times (1-2)\text{Å}^{-1} \times c \sim 10^{-2}\ c$$

$v_F \sim \frac{c}{100}$

$v_s \sim \frac{c}{10{,}000}$

$$v_s \sim \frac{\omega_D}{\pi/a} \sim 10 - 100 \frac{\text{meV}}{\text{Å}^{-1}} \frac{c}{\hbar c} \sim 10^{-2} - 10^{-1} \frac{c}{1000} \sim \frac{c}{10{,}000 - 100{,}000}$$

$\varepsilon_F = 1 \sim 10$ eV

$T_F = 10{,}000 \sim 100{,}000$ K (recall 300 K is 26 meV)

(In comparision, recall $\theta_D \sim 100$ K)

Finite Temperature – Math

Apply standard stat. mech. techniques

Fermi-Dirac function $f(\varepsilon,T)=\frac{1}{e^{\beta(\varepsilon-\mu)}+1}$ $\beta=\frac{1}{k_BT}$

Determine chemical potential μ using $N=\int_0^\infty g(\varepsilon)f(\varepsilon,T)d\varepsilon$ (different from phonon!)

N = number of electrons

Obtain energy from $E=\int_0^\infty \varepsilon g(\varepsilon)f(\varepsilon,T)d\varepsilon$

After some tricky math (Sommerfeld expansion for small T/T_F; see A&M and also homework):

$$\mu \approx \varepsilon_F\left[1-\frac{1}{3}\left(\frac{\pi k_BT}{2\varepsilon_F}\right)^2\right] \qquad \mu(T=0)=\varepsilon_F$$

$$E \approx \frac{3}{5}N\varepsilon_F+\frac{\pi^2}{6}(k_BT)^2g(\varepsilon_F) \qquad g(\varepsilon_F)=\frac{3N}{2\varepsilon_F}$$

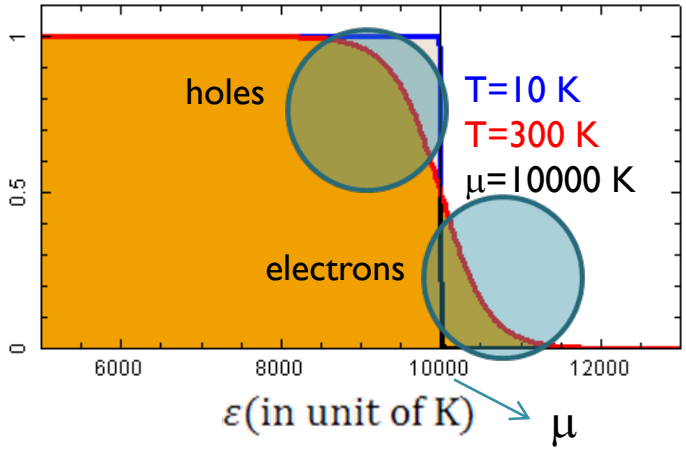
$$C_V=\left(\frac{\partial E}{\partial T}\right)_V=\frac{\pi^2}{3}k_B(k_BT)g(\varepsilon_F)$$

Corrections to T=0 results are of the order, $O\left(\left\{\frac{T}{T_F}\right\}^2\right)$

i.e. very small (10^{-4}) if T ~ RT, compared to T=0 values.

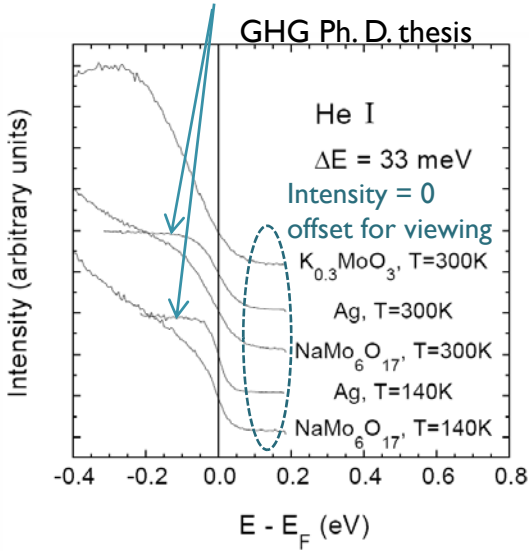
Finite Temperature – Physics

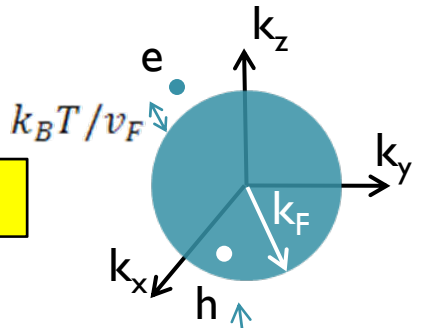
FD function: electron and hole excitation relative to vacuum (i.e. Fermi sea at T = 0)



Deviation from step function (T=0) occurs within the energy range of ~ $k_B T$

Measured FD function





Fermi surface becomes blurry due to many e-h pairs. (only one shown for clarity)

Physics (expressions good up to numerical factors)

Think of excitation rel. to vacuum, not absolute energy.

(1) Energy per excited particle $(A)O(\varepsilon_F)$ $(B)O(k_BT)$ $(C)O((k_BT)^2/\varepsilon_F)$

(2) k_BT/ε_F for T near RT ~ $(A)O(1)$ $(B)\,O(100)$ $(C)O(0.01)$

(3) Number of particles excited $(A)\,g(\varepsilon_F)k_BT$ $(B)N$ $(C)g(\varepsilon_F)(k_BT)^2/\varepsilon_F$

(4) E – E(T=0) $(A)N\varepsilon_F$ $(B)g(\varepsilon_F)(k_BT)^2$ $(C)g(\varepsilon_F)(k_BT)^3/\varepsilon_F$

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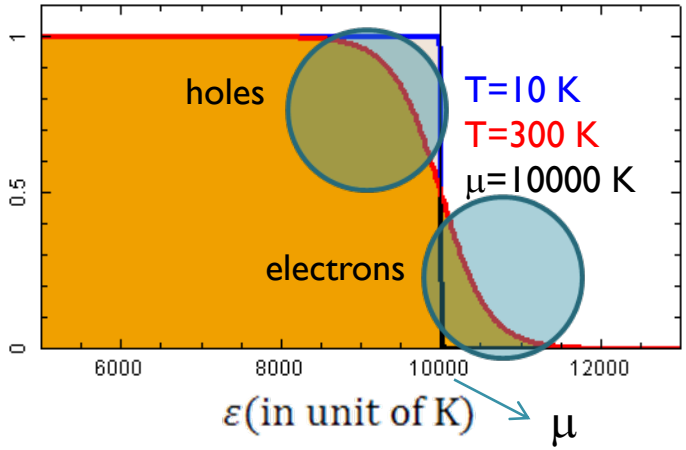

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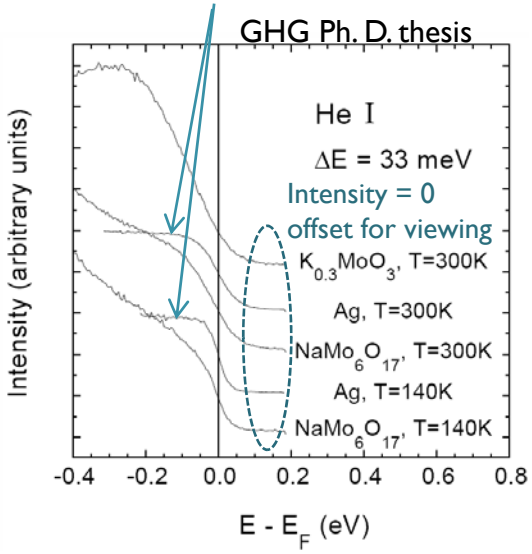

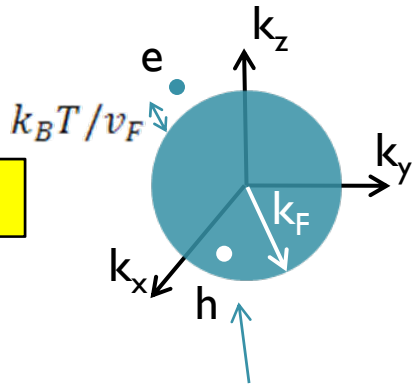

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Think of excitation rel. to vacuum, not absolute energy.

(1) Energy per excited particle ~ $k_B T$
(2) Number of particles ~ $k_B T g(\varepsilon_F)$
(3) E(T) – E(T=0) ~ (1)x(2) ~ $(k_B T)^2 g(\varepsilon_F)$
(4) C(T) = dE/dT ~ $k_B (k_B T) g(\varepsilon_F)$

Heat Capacity due to e⁻'s and lattice

(Often used "specific heat", = heat capacity per volume or mole)

$$C_V(e^-) \approx \frac{\pi^2}{3} k_B (k_B T) g(\varepsilon_F) = \frac{\pi^2}{2} N_e \frac{T}{T_F} k_B \qquad C_V(phonon) \approx \frac{12\pi^4}{5} N_{lattice} \left(\frac{T}{\theta_D}\right)^3 k_B$$

$$C_V \approx \gamma T + \beta T^3$$

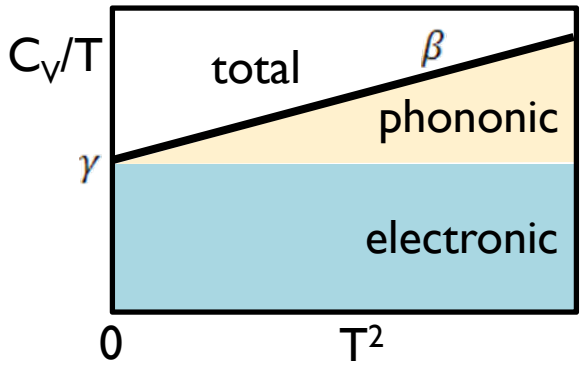
same order in metals

Differences are here!

Phonon term (cube term) is dominant at high (~ room) temperature (θ_D).
Electron term (linear term) is dominant at low temperature.
Rough estimate of the boundary temperaure:

$$\frac{T}{T_F} \sim \left(\frac{T}{\theta_D}\right)^3 \qquad T \sim \theta_D \sqrt{\frac{\theta_D}{T_F}} \sim 100\ K \sqrt{\frac{1}{100}} \sim 10\ K$$

Many Researchers Plot C_V Like this:



$$\frac{C_V}{T} \approx \gamma + \beta T^2$$

γ ~ 1 mJ mol^{-1} K^{-2}
~ free electron value

Many exceptions:
γ can be 1000 times larger!
"Heavy Fermion" system

$$\gamma \sim N_e \frac{k_B}{T_F} \propto m$$

m: effective mass

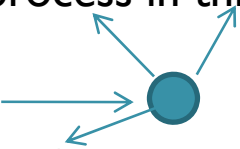
Conduction of Electricity

Source for finite conductivity

NOT ions in static crystal, but impurity, jittering ions (i.e. phonons), and other electrons (but only umklapp process in this case)

A simple model

- Relaxation time τ (time between scattering)
- Scattering events wipe out electron's memory (i.e. restores equilibrium)
- Conduction due to a tiny push by electric field between collisions



Quasi-elastic scattering in random directions

As all electrons are considered free (i.e. independent), we can think as though all electrons go through scattering at the same time.

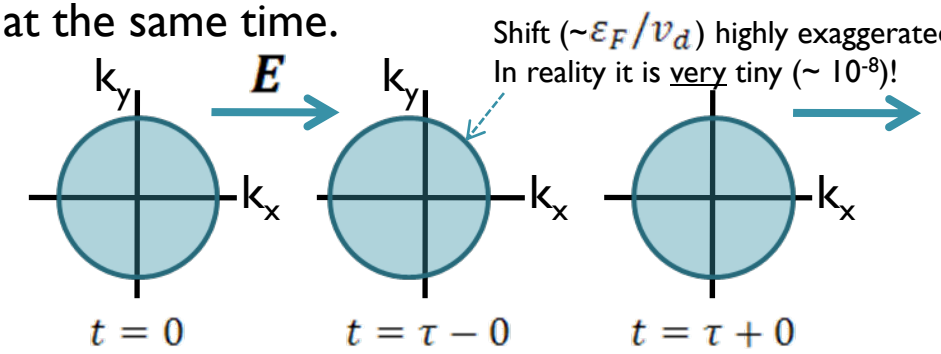
$$F = eE = ma = mv_d/\tau$$

(only magnitude considered)

v_d Drift velocity

NOT electron velocity

Only a small added velocity



Ohm's law

$$j = nev_d = \frac{ne^2\tau}{m}E = \sigma E \qquad \sigma = \frac{ne^2\tau}{m}$$

Drude conductivity=1/Drude resistivity

This solution can be thought of as a steady state solution for an equation.

$$m\left[\frac{dv_d}{dt} + \frac{v_d}{\tau}\right] = F$$

Keep in mind that microscopically, electrons are jittering fast (v_F), and the drift velocity is a tiny fraction (10^{-8} v_F) added to it, but it is what makes a difference since drifting adds up while jittering sums to zero.

We will learn later why ħdk/dt=F which is the reason why we can write like this (just like Newton's law)

Conduction of Electricity

- Two common sources of scattering: e-ph and e-im (ph=phonon, im=impurity)

$$\frac{1}{\tau} = \frac{1}{\tau_{ph}} + \frac{1}{\tau_{im}} = \frac{1}{\tau_{ph}(T)} + \frac{1}{\tau_{im}}$$

Impurity: no T dependence, elastic
Phonon: T dependence, inelastic
(absorption or emission of phonons)

Mattheisen's rule $\rho = \frac{m}{ne^2\tau} = \rho_{ph}(T) + \rho_{im}$

- Units, Time scale, drift velocity etc. in typical metals

$$n \sim \frac{10^{23}}{cm^3} \sim \frac{0.1}{\text{Å}^3}$$

$$\sigma \sim (\mu\Omega\ \text{cm})^{-1} = 10^6(\Omega\ \text{cm})^{-1} = 9.000\text{e}17\ (\text{statOhm} - \text{cm})^{-1} = 9.000\text{e}17\ s^{-1}$$

$$\tau = \frac{m\sigma}{ne^2} = \frac{m\sigma\hbar c}{n\hbar c e^2} \sim \frac{mc^2\sigma\,\hbar c}{n\hbar c c^2 e^2} = \frac{\text{Å}^3\ 0.5e6\ eV\ 9e17\ s^{-1}}{0.1\ 2e3\ eV\ \text{Å}\ 9e36\ \text{Å}^2\ s^{-2}} 137 \sim 3 \times 10^{-14}\ s$$

$$\tau \sim femtosecond\ (R.T.) - 10\ nanosecond\ (low\ T)$$

$$l = v_F\tau = 1e16\frac{\text{Å}}{s} \times \tau \sim 10\ \text{Å} - 1\ \text{mm}$$

Mean free path ~ typically 100 Å – 1 μm

$$v_d = \frac{j}{ne} \sim 1000\frac{\text{A}}{\text{cm}^2}\frac{1}{ne} = \frac{10^3\,\text{A cm}}{10^{23} \times 1.6 \times 10^{-19}\text{C}} \sim 1\frac{\text{mm}}{s} \sim 10^{-11}c \sim 10^{-9}v_F$$

Drift Velocity – Slow!

Conduction of Heat

Heat current = $-\frac{1}{3}vl\frac{d(\frac{E}{V})}{dz} = -\frac{1}{3}vl\frac{dE}{V\,dT}\frac{dT}{dz} \equiv -\kappa\frac{dT}{dz}$

Thermal conductivity $\kappa = \frac{1}{3}vl\frac{C}{V}$

$C = \frac{\pi^2}{2}N\frac{k_BT}{k_BT_F}k_B$

Fermi velocity $v = v_F$

Electron heat capacity

Electron mean free path $l = v_F\tau$

$k_BT_F = \varepsilon_F = \frac{1}{2}mv_F^2$

$$\kappa = \frac{1}{3}vl\frac{C}{V} = \frac{1}{3}v_F^2\tau\frac{\pi^2}{2}\frac{N}{V}\frac{k_BT}{\frac{1}{2}mv_F^2}k_B = \frac{\pi^2}{3}n\tau\frac{k_B^2T}{m} = \frac{\pi^2}{3}\frac{n\tau}{m}k_B^2T \qquad n = \frac{N}{V}$$

$$\sigma = \frac{ne^2\tau}{m}$$

Physics: transport efficiency is high if there are many carriers (n) with long relaxation time (τ), light mass (m^{-1}).

So, it may not come as a surprise …

Wiedemann-Franz Law

$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$ ≡ Lorenz number

"Universal" constant

Holds as long as scattering is elastic or quasi-elastic (energy change << k_BT). Ok for impurity scattering (low T) or when T >> θ_D (high T).
It breaks down at intermediate T (read p. 92-96)

Reading