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Electrons in metals.

- In metals the Coulomb repulsion between electrons is screened and effectively the electrons can be treated as non-interacting fermions forming an ideal gas.
- However, N/V is large and T is small compared with the characteristic temperature T_F (Fermi temperature) so we cannot treat it as an non-degenerate ideal gas.

  Quantum effects are very important.

Since electrons have spin 1/2 they are fermions and we will use F-D statistics.

We know

$$\bar{n}_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1} \qquad (1)$$

μ : chemical potential $\equiv$ Fermi energy

μ is determined by requiring that

$$\sum_s \bar{n}_s = N = \sum_s \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1}$$ then $\mu = \mu(T)$.

Fermi function:

$$F(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$

$\varepsilon : 0$ to ∞

(ε is assume continuous since $\Delta\varepsilon_s \ll 1$).

If $\beta\mu \ll 0 \Rightarrow \mu < 0$ (no problem since $\mu < 0$ for the ideal gas).

$$F(\varepsilon) \simeq e^{-\beta(\varepsilon-\mu)}$$

Maxwell-Boltzmann behavior which occurs for high T and low N/V.

But if $\beta\mu = \frac{\mu}{kT} >> 1$ low T regime

Then $\mu > 0$ Is this a problem?

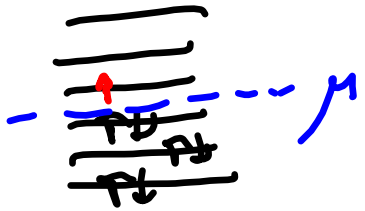
$dG = TdS - pdV + \mu dN$

then

$$\mu = \frac{\partial E}{\partial N}\Big|_{S,V}$$

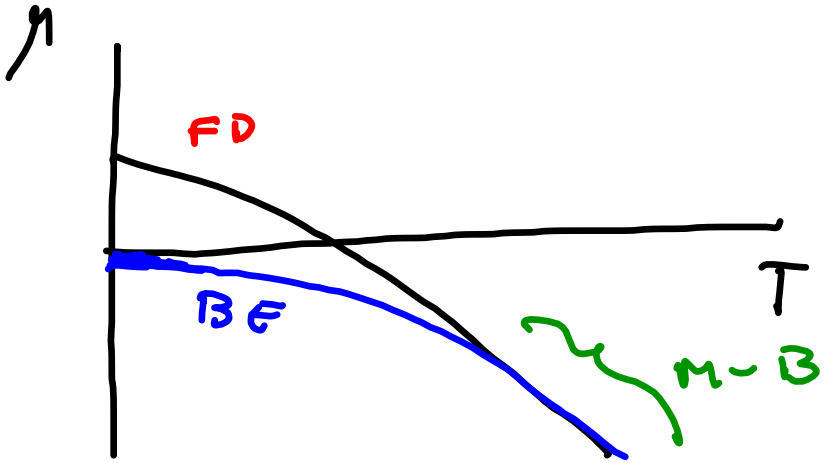
- For an ideal gas if I add a particle the entropy will increase. The only way of adding one particle keeping S constant is by reducing E.
  Then $\mu < 0$.

• For fermions at $T=0$



} we still have 1 single accessible state. Thus $S=0$ = constant

and $\left.\frac{\partial E}{\partial N}\right|_{S,V} > 0 \therefore \mu > 0.$

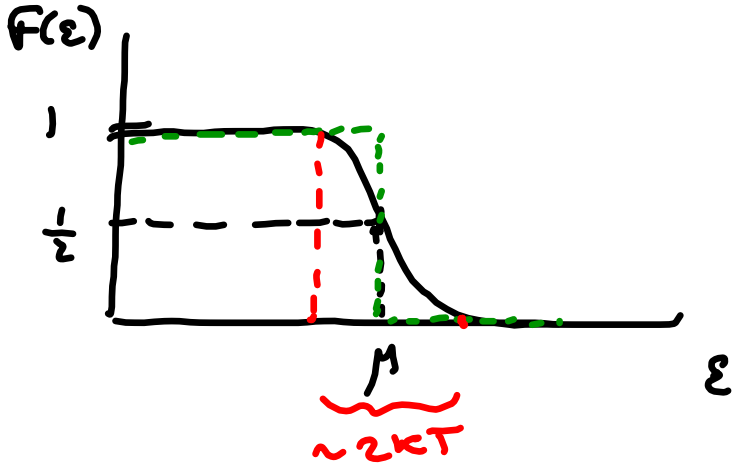


For fermions if $\beta\mu >> 1$: $f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$

if $\varepsilon << \mu \Rightarrow \beta(\varepsilon-\mu) << 0 \quad \therefore \quad F(\varepsilon) = 1$

if $\varepsilon >> \mu \Rightarrow \beta(\varepsilon-\mu) >> 0 \quad \therefore \quad F(\varepsilon) = e^{-\beta(\varepsilon-\mu)} \to 0.$

if $\varepsilon = \mu \Rightarrow \beta(\varepsilon-\mu) = 0 \quad \therefore \quad F(\varepsilon) = \frac{1}{2}$



— $T > 0$

— $T = 0$

At $T=0$ all the levels below μ are filled by 2 electrons each (one with spin $\uparrow$ and one with spin $\downarrow$).

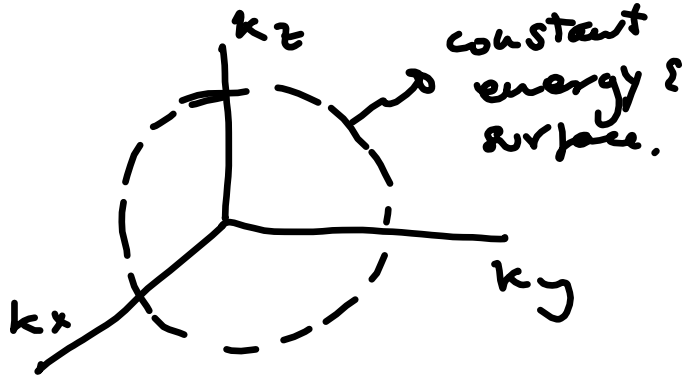
$T=0$:

Let's find μ_0 (Fermi energy at $T=0$).

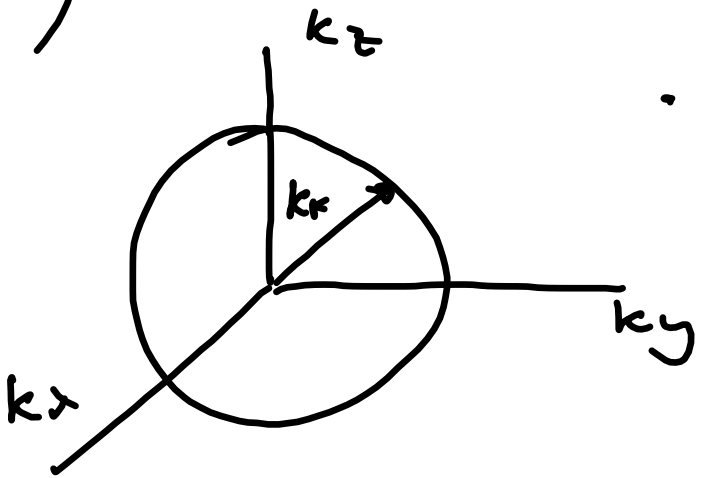
$$\varepsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

If $\varepsilon = \mu_0$ then

$$\mu_0 = \frac{\hbar^2 k_F^2}{2m}$$



$\Delta t \quad \mathcal{E} = \mu_0$



- States with $k \leq k_F$ are occupied.
- States with $k > k_F$ are empty.

In order to calculate the number of states inside the "Fermi sphere" we have to obtain the energy levels for the electrons.

Assume PBC for a particle in a box:

$$\psi(x_i) = \psi(x_i + L_i) \Rightarrow e^{i k_i \cdot L_i} = 1$$

$$k_i \cdot L_i = 2\pi n_i \quad \text{or} \quad k_i = \frac{2\pi n_i}{L_i} \qquad n_i = 0, \pm 1, \pm 2, \ldots$$

Solutions: plane waves.

$$\Delta n_i = \frac{L_i}{2\pi} dk_i \qquad V = L_x L_y L_z$$

Δ # of states in the k interval $k_i, k_i + dk_i$

Then

$$\rho d^3k = \Delta n_x \Delta n_y \Delta n_z = \frac{V}{(2\pi)^3} d^3k$$

# of states between $\vec{k}, \vec{k} + d^3\vec{k}$

Then at $T=0$ the total number of (populated) states in k space is:

$$\int_0^{k_F} k^2 dk \frac{V}{(2\pi)^3} \underbrace{\int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\varphi}_{4\pi} = \frac{4\pi V}{(2\pi)^3} \frac{1}{3} k_F^3$$

$$= \frac{4}{3}\pi k_F^3 \frac{V}{(2\pi)^3}$$

But since the electrons have 2 spin projections there are 2 electrons occupying each state inside the sphere, then

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

Then

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

We can define

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

de Broglie wavelength at k_F.

If $\lambda = \frac{2\pi}{k} > \lambda_F$ the state is occupied.

If $\lambda = \frac{2\pi}{k} < \lambda_F$ " " " empty.

From (1) since

$$\mu_0 = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3}$$

Fermi temperature:

$$T_F = \frac{\mu_0}{k} \approx 80{,}000\,K \quad \text{for Cu.}$$

T_F is very high for ordinary metals and then room temperature ($T \sim 300\,K$) $\ll T_F$. Then we always need to use the degenerate Fermi-Dirac gas to study electrons.

So at $T = 300\,K$ $\mu(T) \sim \mu_0$.

Consequences of F-D in observables:

Heat capacity:

$$C_V = \frac{\partial \bar{\varepsilon}}{\partial T}\Big|_V$$

For M-B: $C_V = \frac{3}{2}Nk$ (constant) (since $\bar{\varepsilon} = \frac{3}{2}NkT$)

But now only the energy of the few electrons within kT of μ_0 can change with temperature (the other ones are unable to change levels).

$N_{eff} \approx \rho(\mu)\, kT$ effective # of electrons that can change their energy as T changes.

$$C_V = N_{eff}\frac{3}{2}k = \rho(\mu)\,kT\,\frac{3}{2}k = \frac{3}{2}\rho(\mu)k^2T \propto T!$$

Notice that $N_{eff} \sim \frac{kT}{\mu}N$

$$C_V = \frac{kT}{\mu}N\frac{3}{2}k = \frac{3}{2}\underbrace{\frac{k^2}{\mu}}_{kT_F}NT = \frac{3}{2}\underbrace{kN}_{\nu R}\frac{T}{T_F} =$$

$$= \frac{3}{2}\nu R\underbrace{\frac{T}{T_F}}\ \text{very small.}$$

Explains why it is hard to see the difference in C_V between metals and insulators

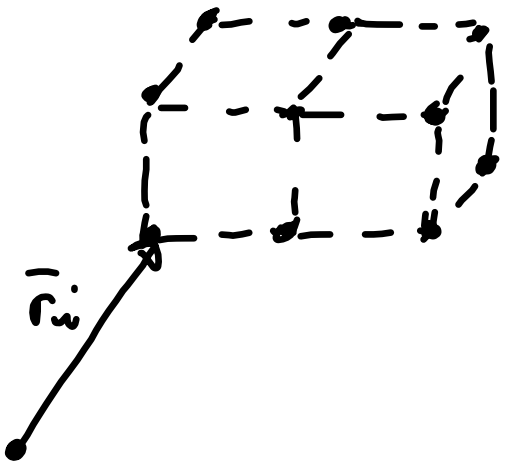
Both in metals and insulators most of C_V is due to the change in energy with T of the lattice vibrations - That C_V goes like T^3 (as we will see).

Read 9.17 to see how to calculate C_V for the electrons quantitatively.

Ch. 10:

Interacting Systems.

Solids:



- N atoms at $\bar{r}_i$ with mass m_i
- In equilibrium the ions are at $\bar{r}_i = \bar{r}_i^{(0)}$.
- Each ion vibrates about $\bar{r}_i^{(0)}$.

$\bar{r}_i = (x_i, y_i, z_i)$ $\quad x_{i\alpha}$ $\quad \alpha = 1, 2, 3$ (x, y, z)

Let's define

$$\xi_{i\alpha} = x_{i\alpha} - x_{i\alpha}^{(0)} \qquad \alpha = 1,2,3$$

$$K = \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3} m_i \dot{x}_{i\alpha}^2 = \frac{1}{2}\sum_{i=1}^{N}\sum_{\alpha=1}^{3} m_i \dot{\xi}_{i\alpha}^2$$

ξ kinetic energy of vibration

$$V = V(x_{11}, x_{12}, x_{13}, \ldots, x_{N3})$$ potential energy involves all the coordinates.

We can expand V in a Taylor series about the equilibrium position:

$$V = V_0 + \sum_{i,\alpha} \frac{\partial V}{\partial x_{i\alpha}}\bigg|_{x_{i\alpha}^{(0)}} \xi_{i\alpha} + \frac{1}{2} \sum_{\substack{i,\alpha \\ j,\beta}} \underbrace{\frac{\partial^2 V}{\partial x_{i\alpha}\partial x_{j\beta}}\bigg|_0}_{A_{i\alpha,j\beta}} \xi_{i\alpha}\xi_{j\beta} + \cdots$$

$\frac{\partial V}{\partial x_{i\alpha}}\big|_{x_{i\alpha}^{(0)}} = 0$

$A_{i\alpha,j\beta}$ tensor of rank 2, $3N \times 3N$ matrix

$$\simeq V_0 + \frac{1}{2} \sum_{i\alpha,j\beta} A_{i\alpha,j\beta}\,\xi_{i\alpha}\xi_{j\beta}$$

$$\mathcal{H}_{vibr} = V_0 + \frac{1}{2}\sum_{i\alpha} m_i \dot{\xi}_{i\alpha}^2 + \frac{1}{2} \sum_{i\alpha,j\beta} A_{i\alpha,j\beta}\xi_{i\alpha}\xi_{j\beta}$$

We can make a change of basis so that $A_{i\alpha,j\beta}$ becomes diagonal.

Generalized coordinates $q_r (r = 1, 2, \ldots, 3N)$ given by:

$$q_r = \sum_{i=1}^{N} \sum_{\alpha=1}^{3} C_{r,i\alpha} \xi_{i\alpha}$$

or inverting the transformation

$$\xi_{i\alpha} = \sum_{r=1}^{3N} B_{i\alpha,r} q_r$$

$B_{i\alpha,r}$ are such that $A_{i\alpha,j\beta} = \omega_r$ (Diagonal)

Then

$$\mathcal{H} = V_0 + \frac{1}{2} \sum_{r=1}^{3N} (\dot{q}_r^2 + \omega_r^2 q_r^2)$$

ω_r are the 3N frequencies of vibration for the normal modes of the solid