

## Lecture 6

We have derived second-quantized Hamiltonian for interacting electrons in a crystal:

$$H = \int d\vec{r} \sum_{\alpha} \Psi_{\alpha}^{\dagger}(\vec{r}) \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi_{\alpha}(\vec{r}) + \frac{1}{2} \int d\vec{r}^{\dagger} d\vec{r}^{\dagger'} \sum_{\alpha\alpha'} \cancel{\Psi_{\alpha}^{\dagger}(\vec{r}^{\dagger}) \Psi_{\alpha'}(\vec{r}^{\dagger'})} V(\vec{r}^{\dagger} - \vec{r}^{\dagger'}) \Psi_{\alpha}^{\dagger}(\vec{r}^{\dagger}) \Psi_{\alpha'}^{\dagger}(\vec{r}^{\dagger'}) \cdot \Psi_{\alpha}(\vec{r}) \Psi_{\alpha'}(\vec{r}')$$

As I mentioned, this problem can't be solved exactly and we must use approximations. The "art" of solid state physics is to find the simplest approximation that still captures the essence of the problem.

Remarkably, the ~~simplest~~ <sup>crudest</sup> possible approximation—neglecting both crystal potential and interactions—captures the ~~most~~ basic properties of some solids (metals) remarkably well. This model is known as free electron model or Sommerfeld model. I have already mentioned parts of it in lecture 2. Now we will look at it in more detail.

Free noninteracting electron Hamiltonian ~~is~~ is:

$$H = \int d\vec{r} \sum_{\alpha} \Psi_{\alpha}^{\dagger}(\vec{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \Psi_{\alpha}(\vec{r})$$

It is diagonalized by transforming to plane-wave single-particle basis:

$$\Psi_0^+(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{k}} e^{-i\vec{k} \cdot \vec{r}} c_{\vec{k}\sigma}^+$$

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$$H = \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} c_{\vec{k}\sigma}^+ c_{\vec{k}\sigma}$$

$$\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$$

The ground state is the Fermi sea:

$$|\Psi_0\rangle = \prod_{\vec{k} < k_F, \sigma} c_{\vec{k}\sigma}^+ |0\rangle$$

The Fermi momentum is determined by counting the total number of filled states and setting it equal to the number of electrons.

$$2 \cdot \frac{4\pi k_F^3}{3} \cdot \frac{1}{\underbrace{(2\pi)^3}_V} = \frac{V}{3\pi^2} k_F^3 = N$$

$$k_F = (3\pi^2 n)^{1/3}$$

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

let's look at thermodynamic properties of the Fermi sea at finite temperature.

All thermodynamic quantities can be calculated from the partition function:

$$Z = \text{Tr} e^{-\frac{H - \mu N}{k_B T}}$$

Need to subtract  $\mu N$  from the Hamiltonian if we want to keep the chemical potential instead of the particle numbers fixed - usually more convenient.

$$H - \mu N = \sum_{k\sigma} (\epsilon_k - \mu) c_{k\sigma}^\dagger c_{k\sigma}$$

The  $\text{Tr}$  (trace) means sum over diagonal matrix elements:

$$\begin{aligned} Z &= \sum_{\{n\}} \langle \{n\} | e^{-\frac{H - \mu N}{k_B T}} | \{n\} \rangle = \\ &= \prod_{k\sigma} \sum_{n_{k\sigma}=0,1} e^{-\frac{(\epsilon_k - \mu) n_{k\sigma}}{k_B T}} = \\ &= \prod_{k\sigma} \left( 1 + e^{-\frac{\epsilon_k - \mu}{k_B T}} \right) \end{aligned}$$

Given  $Z$ , we can calculate the free energy:

$$\begin{aligned} \Omega &= -k_B T \ln Z = -k_B T \ln \prod_{k\sigma} \left( 1 + e^{-\frac{\epsilon_k - \mu}{k_B T}} \right) = \\ &= -2 k_B T \sum_k \ln \left( 1 + e^{-\frac{\epsilon_k - \mu}{k_B T}} \right) \end{aligned}$$

Calculate the total number of particles, given the chemical potential  $\mu$ .

$$N = - \left( \frac{\partial \Omega}{\partial \mu} \right)_T$$

$$N = \sum_k \frac{2 k_B T \frac{1}{k_B T} e^{-\frac{\epsilon_k - \mu}{k_B T}}}{1 + e^{-\frac{\epsilon_k - \mu}{k_B T}}} =$$

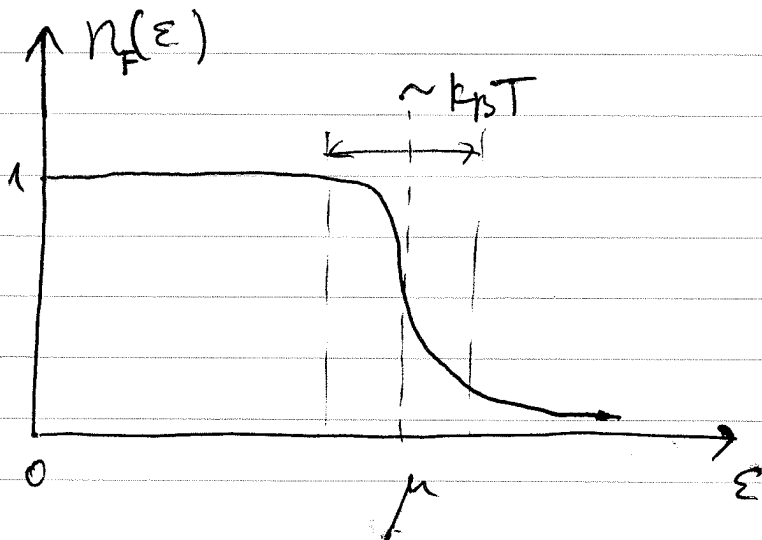
$$= 2 \sum_k \frac{1}{e^{\frac{\epsilon_k - \mu}{k_B T}} + 1} = \sum_{k\sigma} \frac{1}{e^{\frac{\epsilon_k - \mu}{k_B T}} + 1}$$

Thus, the average number of particles in a state  $k\sigma$  at temperature  $T$  is given by:

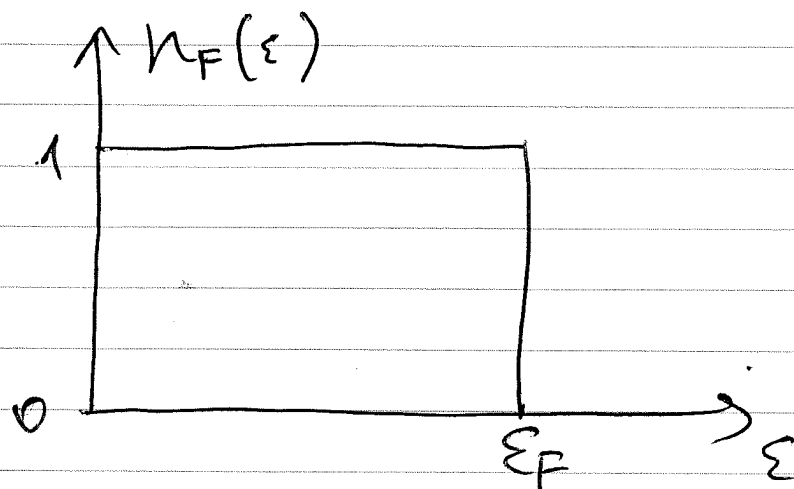
$$n_{k\sigma} = \frac{1}{e^{\frac{\epsilon_k - \mu}{k_B T}} + 1} \quad - \text{Fermi-Dirac distribution.}$$

This is very different from the Boltzmann distribution for classical particles:

$$n_k \sim e^{-\frac{\epsilon_k - \mu}{k_B T}}$$



At  $T=0$  the distribution becomes step-line:



Compare typical thermal energy scales with  $\epsilon_F$ .

$$\epsilon_F \sim 1-10 \text{ eV.}$$

Take  $T = 300 \text{ K}$  - room temperature

$$k_B = 1.38 \cdot 10^{-16} \text{ erg} \cdot \text{K}^{-1}$$

$$k_B T \sim 4 \cdot 10^{-14} \text{ erg}$$

$$1 \text{ eV} = 1.6 \cdot 10^{-12} \text{ erg}$$

$$k_B T \sim 10^{-2} \text{ eV} - \text{much smaller than } \epsilon_F.$$

Thus the broadening of  $n_F(\epsilon)$  is typically very small and  $\mu \approx \epsilon_F$ .

Calculate specific heat of the Fermi sea.

In classical statistical mechanics:

change in energy <sup>density</sup> of the gas as the temperature

is increased by  $\Delta T$  is:

$$\Delta \varepsilon = \frac{3}{2} n k_B T$$

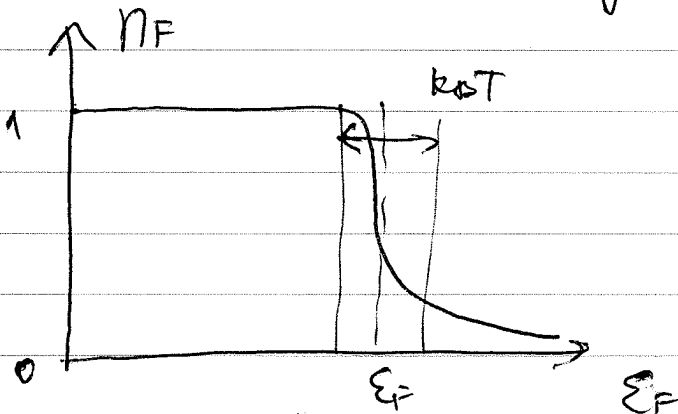
$$C_V = \frac{\Delta \varepsilon}{\Delta T} = \frac{3}{2} n k_B$$

Thus classical statistical mechanics predicts constant specific heat per volume, proportional to the density  $n$ .

This is not what is observed in metals:

$C_V \sim k_B T$  - becomes very small at low temperatures.

The reason is Pauli principle.



In a metal only electrons within a narrow strip of width  $\sim k_B T$  around the Fermi energy can absorb any ~~amount~~ heat:

$$\Delta \varepsilon \sim k_B T n \frac{k_B T}{E_F}$$

$$C_V \sim k_B n \frac{k_B T}{E_F}$$

To ~~calculate~~ calculate specific heat need  
to calculate the total internal energy of the electrons.

~~calculate~~

$$U = \sum_{\vec{k}, \sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} = 2 \sum_{\vec{k}} \epsilon_{\vec{k}} n_F(\epsilon_{\vec{k}})$$

Energy per volume:

$$u = \frac{U}{V} = \frac{2}{V} \sum_{\vec{k}} \epsilon_{\vec{k}} n_F(\epsilon_{\vec{k}})$$

$$C_V = \left( \frac{\partial u}{\partial T} \right)_V$$

$$\frac{1}{V} \sum_{\vec{k}} \leftrightarrow \int \frac{d^3 \vec{k}}{(2\pi)^3}$$

$$u = \int \frac{d^3 \vec{k}}{4\pi^3} \epsilon_{\vec{k}} n_F(\epsilon_{\vec{k}})$$

Since the integrand only depends on  $k^2$  through  
the energy  $\epsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$ , it is convenient to

transform the integral over  $\vec{k}$  into an integral over  $\epsilon$ .

$$d\vec{k} = k^2 dk \sin \theta d\theta d\varphi$$

Since  $\epsilon_{\vec{k}}$  doesn't depend on the direction of  $\vec{k}$ ,  
we can integrate over  $\theta$  and  $\varphi$ . The integral gives  $4\pi$ .

$$d\vec{k} = 4\pi k^2 dk$$

Express  $n(\vec{k})$  in terms of  $\epsilon_k$ :

$$\epsilon_k = \frac{\hbar^2 k^2}{2m}$$

$$k = \frac{\sqrt{2m\epsilon_k}}{\hbar}$$

$$dk = \frac{1}{\hbar} \sqrt{\frac{m}{2}} \frac{d\epsilon}{\sqrt{\epsilon}}$$

$$4\pi k^2 dk = 4\pi \cdot \frac{2m\epsilon}{\hbar^2} \cdot \frac{1}{\hbar} \sqrt{\frac{m}{2}} \frac{d\epsilon}{\sqrt{\epsilon}} =$$

$$= \frac{4\pi m}{\hbar^2} \sqrt{\frac{m\epsilon}{2}} d\epsilon$$

Then the expression for  $n$  becomes:

$$n = \int_0^{\infty} d\epsilon \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2m\epsilon}{\hbar^2}} \epsilon n_F(\epsilon)$$

$$g(\epsilon) = \frac{m}{\pi^2 \hbar^2} \sqrt{\frac{2m\epsilon}{\hbar^2}} \quad - \text{density of states.}$$

Physical meaning:  $g(\epsilon) d\epsilon$  = number of single-electron states in the energy interval  $(\epsilon, \epsilon + d\epsilon)$  per unit volume.