Anisotropic Fermi gas

For metals we have partially filled bands. Electronic properties of such materials if interelectron interaction is neglected is very similar to that of a noninteracting Fermi gas. The only differences are that the electron energy $\mathcal{E}(p)$ is not in general equal to $\frac{p^2}{2m}$ and we should take band filling into account.

The energy spectrum $\mathcal{E}(p)$ is strongly simplified if we have almost empty band. Near the bottom of the band we can expand $\mathcal{E}(p)$ for small p. For a cubic crystal we obtain

$$\mathcal{E}(p) = \mathcal{E}_0 + \frac{p^2}{2m^*}$$

We derived this result in the previous lecture for the tight binding model but isotropy of the spectrum follows from general symmetry arguments. Effective mass tensor $m_{\alpha\beta}$ being symmetric rank 2 tensor $\propto \delta_{\alpha\beta}$

We have very similar picture for almost filled band. More convenient objects to deal with are <u>holes</u> rather than electrons. These holes are concentrated near the maximum of the energy. Expanding near it for cubic crystal we obtain

$$\mathcal{E}(p) = \mathcal{E}_0 - \frac{p^2}{2m^*}$$

This formula is not very convenient because electron's effective mass appears to be negative. However if we consider holes and count their energy from the top of the band we should change sign for both charge e and energy $\mathcal{E}$. Than they will have positive mass m^*.

Note that metalls with small number of electrons or holes are rather rare. Indeed for typical metal with odd number of electrons per primitive cell we have half filled band.

In order to have small carrier number one should have even number of electrons per cell and small overlap of two upper bands.

E ↑

E_F

k
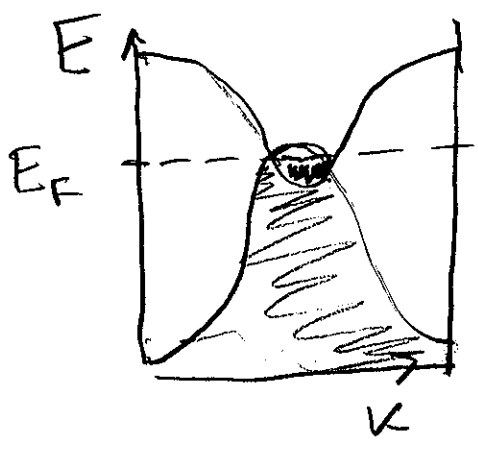
Then instead of complete filling of the lower band it is energetically favorable to put same number of electrons to the upper conduction band leaving the same number of holes in the lower valence band. This happens in semimetals like Bi, Sb, As, graphite.

Another situation may happen in nonstochiometric compounds that are doped AB_x with $x \ll 1$. In this example conduction electrons are coming from small amount of B atoms if A compound is insulator. That is what happens in high temperature superconductors.

Density of states

The density of states is the number of electron states per unit volume

$$N(E) = \sum_{p,s} \delta(E - \mathcal{E}(p)) =$$

$$= 2 \int \frac{d^3p}{(2\pi\hbar)^3} \delta(E - \mathcal{E}(p))$$

Contrary to the conventional Fermi gas we cannot replace $\mathcal{E}(p)$ by $\frac{p^2}{2m}$ and perform the integration. We do the following: Consider the surface in momentum space $\mathcal{E}(p) = $ const. Then the integration d^3p can be replaced by $d^3p = dS\, dp_n$, where dS surface element and dp_n is integration over ortogonal to that surface component of p. But $dp_n = \dfrac{d\mathcal{E}}{|\partial\mathcal{E}/\partial p|} =$

$$= \frac{d\mathcal{E}}{|\mathcal{U}(p)|}$$

Then $N(E) = \dfrac{2}{(2\pi\hbar)^3} \int \dfrac{d\mathcal{E}\, dS}{|\mathcal{U}(p)|} \delta(E - \mathcal{E}(p))$

$$N(E) = \frac{2}{(2\pi\hbar)^3} \int_{\mathcal{E}=E} \frac{dS}{|\mathcal{U}(p)|}$$

Specific heat

Internal energy of the anisotropic Fermi gas is

$$E = 2V \int \varepsilon(p) f \frac{d^3p}{(2\pi\hbar)^3} \, ,$$

where f is Fermi function

$$f = \frac{1}{\exp[(\varepsilon - M)/T] + 1}$$

and factor 2 comes from two spin components

Specific heat is then

$$C = \frac{1}{V}\left(\frac{\partial E}{\partial T}\right)_V = 2 \int \varepsilon(p) \frac{\partial f}{\partial T} (d^3p)$$

$$\frac{\partial f}{\partial t} = \frac{1}{T} \frac{e^{(\varepsilon - M)/T}}{\left(e^{(\varepsilon - M)/T} + 1\right)^2}\left(\frac{\varepsilon - M}{T} + \frac{dM}{dT}\right)$$

For fixed electron density we should take temperature dependence of chemical potential into account.

Since

$$\frac{\partial f}{\partial \varepsilon} = -\frac{1}{T} \frac{e^{\frac{\varepsilon - \mu}{T}}}{\left(e^{\frac{\varepsilon - \mu}{T}} + 1\right)^2}$$

we can replace

$$\frac{\partial f}{\partial T} = -\frac{\partial f}{\partial \varepsilon}\left(\frac{\varepsilon - \mu}{T} + \frac{d\mu}{dT}\right)$$

We get $\frac{d\mu}{dT}$ from the condition $\frac{\partial}{\partial T}\frac{N_e}{V} = 0$

$$\frac{\partial}{\partial T}\frac{N_e}{V} = 2 \int \frac{\partial f}{\partial T} \frac{d^3 p}{(2\pi\hbar)^3}$$

Substituting $\frac{\partial f}{\partial t}$ we obtain

$$-2 \int \frac{\partial f}{\partial \varepsilon}\left(\frac{\varepsilon - \mu}{T} + \frac{d\mu}{dT}\right)\frac{d^3 p}{(2\pi\hbar)^3} = 0 \quad \text{and}$$

$$C = -2 \int \varepsilon \frac{\partial f}{\partial \varepsilon}\left(\frac{\varepsilon - \mu}{T} + \frac{d\mu}{dT}\right)\frac{d^3 p}{(2\pi\hbar)^3}$$

For $T \ll \mu(0)$ $\frac{\partial f}{\partial \varepsilon}$ is nonzero in a narrow region $\sim T$ around the Fermi surface

Replacing $\dfrac{d^3p}{(2\pi\hbar)^3} = \dfrac{2}{(2\pi\hbar)^3} \displaystyle\int \dfrac{d\varepsilon \, ds}{|\sigma(p)|} = N(\varepsilon)\,d\varepsilon$

we obtain

$$C = -2 \int \varepsilon \frac{\partial f}{\partial \varepsilon} \left(\frac{\varepsilon - \mu}{T} + \frac{d\mu}{dT} \right) N(\varepsilon)\,d\varepsilon$$

$$\int \frac{\partial f}{\partial \varepsilon} \left(\frac{\varepsilon - \mu}{T} + \frac{d\mu}{dT} \right) N(\varepsilon)\,d\varepsilon = 0$$

We have to evaluate integrals of type

$$\int F(\varepsilon) \frac{\partial f}{\partial \varepsilon}\, d\varepsilon$$

But $\dfrac{\partial f}{\partial \varepsilon}$ is nonzero only near $\varepsilon = \mu$.

Then we can expand $F(\varepsilon)$

$$F(\varepsilon) = F(\mu) + (\varepsilon - \mu) F'(\mu) + \frac{(\varepsilon - \mu)^2}{2} F''(\mu) + \dots$$

Expression for $\dfrac{\partial f}{\partial \varepsilon}$ can be rewritten as

$$\frac{\partial f}{\partial \varepsilon} = - \frac{1}{4T \cosh^2\left(\frac{\varepsilon - \mu}{2T} \right)}$$

It is even function of $\varepsilon-\mu$ that decays very fast. Then odd terms in the expansion for $F(\varepsilon)$ will give zero after integration.

Remaining integrals are

$$\int \frac{\partial f}{\partial \varepsilon} d\varepsilon = 1$$

$$\int (\varepsilon-\mu)^2 \frac{\partial f}{\partial \varepsilon} d\varepsilon = -\frac{1}{4T} \int_{-\infty}^{\infty} \frac{z^2 dz}{\cosh^2\left(\frac{z}{2T}\right)} = -\frac{\pi^2 T^2}{3}$$

Thus we get

$$\int F(\varepsilon) \frac{\partial f}{\partial \varepsilon} d\varepsilon \approx -F(\mu) - \frac{\pi^2 T^2}{6} F''(\mu)$$

Applying it to expressions for C and $\frac{\partial}{\partial T} \frac{N_e}{V}$ we obtain

$$C = \mu N(\mu) \frac{d\mu}{dT} + \frac{\pi^2 T}{3} \frac{d}{d\mu} \mu N(\mu)$$

$$\frac{\partial}{\partial t} \frac{N_e}{V} = N(\mu) \frac{d\mu}{dT} + \frac{\pi^2 T}{3} \frac{\partial N(\mu)}{\partial \mu} = 0$$

From the last equation we obtain

$$\frac{dM}{dT} = -\frac{\pi^2 T}{3} \frac{N'(\mu)}{N(\mu)} \implies \mu(T) = \mu(0) - \frac{\pi^2 T^2}{6} \frac{N'(\mu)}{N(\mu)}$$

Substituting it into expression for C

we arrive at

$$C = \frac{\pi^3}{3} T N(\mu)$$

The physical meaning of this formula is the following: Only electrons in a narrow region around the Fermi surface are important for thermal excitations. Their number is $\sim$ T $\cdot$ N(μ). Each of them gives ~ 1 to the specific heat.

The linear temperature dependence of specific heat is typical property of metals

For isotropic metal

$$N(\mu) = \frac{2}{(2\pi\hbar)^3} \int \frac{dS}{|v|} = \frac{2}{(2\pi\hbar)^3} \frac{4\pi p_F^2}{p_F/m^*} = \frac{p_F m^*}{\pi^2 \hbar^3} =$$

$$\Rightarrow C = \frac{p_F m^*}{3\hbar^3} T = \gamma T,$$

$$\gamma = \frac{p_F m^*}{3\hbar^3}$$

Effective mass can strongly vary from metal to metal. It is about

$$m^* \sim \frac{p_F^2}{\Delta \varepsilon} \,, \text{ where } \Delta \varepsilon \text{ is the band width}$$

For transition metals that have not filled inner d-orbitals their overlapping is small. Tight binding approximation is the good one. Their specific heat may be order of magnitude bigger than for other metals