PHYS 3014: Statistical Mechanics

Lecture Notes
Part 23

Electron Gas in Metal, Specific Heat & Liquid Helium

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Electron gas in metal : specific heat of Metals

To a first approximation, the mutual interactions among electrons in metal are neglected. The electrons in metal can be treated as an ideal gas. These are valence electrons of atoms of the metal and are loosely bound. They can move freely throughout the whole volume of metal. The positive ion cores are confined to near vicinity of their lattice points. This is called free electron theory of metal.

The electrons have spin $\frac{1}{2}$, so free electron gas can be treated as ideal Fermi gas obeyin Fermi-Dirac statistics. In other words, the electrons in a metal can be treated as a non-interacting gas of fermions.

The mean number of particles i.e electrons in a state i with energy ϵ_i is

$$\bar{n}_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1} \quad --- \text{(1)}$$

The quantity μ is called the Fermi energy of the system.
Total no of electrons N in the volume V is

$$N = \sum_i \bar{n}_i \quad \text{--- (2)}$$

We define Fermi function as

$$F(\epsilon) \equiv \frac{1}{e^{\beta(\epsilon-\mu)}+1} \quad \text{--- (3)}$$

The lowest value of ϵ is zero. If μ is such that $\beta\mu << 0$, then $e^{\beta(\epsilon-\mu)} >> 1$, so $F(\epsilon)$ reduces to M-B distribution.

If $\beta\mu >> 1$ i.e at low temperature and $\epsilon << \mu$ then $\beta(\epsilon-\mu) << 0$

$$\therefore \quad F(\epsilon) = 1$$

On the other hand if $\epsilon >> \mu$ then $\beta(\epsilon-\mu) >> 0$

$$\therefore \quad F(\epsilon) = e^{\beta(\mu-\epsilon)}$$ i.e $F(\epsilon)$ falls off exponentially like M-B distribution.

If $\epsilon = \mu$, then $F(\epsilon) = \frac{1}{2}$. The transition region in which $F(\epsilon)$ goes from a value close to 1 to a value close to zero corresponds to an energy interval of the order of KT around $\epsilon = \mu$. When $T \to 0$, $\beta \to \infty$, so the transition region becomes infinitesimally narrow. In such situation

$$F(\epsilon) = 1 \quad \text{for } \epsilon < \mu$$
$$= 0 \quad \text{for } \epsilon > \mu$$

The density of free electrons in metal is very high. The fermi energy of metals are of the order of several eV. Therefore, Fermi temperature defined as $T_F = \frac{\text{Fermi energy}}{K}$ is also very high in comparison to room temperature. It means that free electrons in metals is highly degenerate at room temperature. The electron gas in metal can be treated as a degenerate ideal fermi gas

We can calculate Fermi energy of the gas at 0 K.

we know that

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

At T = 0 all states are filled up to fermi level. Fermi level corresponds to Fermi momentum p_f.

$$E_F = \frac{p_f^2}{2m} = \frac{\hbar^2 k_f^2}{2m}$$

All states with $k < k_f$ are filled and those with $k > k_f$ are empty.

Volume of sphere of radius k_f in k-space is

$$\frac{4}{3}\pi k_f^3$$

There are $\frac{V}{(2\pi)^3}$ translational states per unit volume in k-space so the Fermi sphere of radius k_f contains $\frac{V}{(2\pi)^3}\cdot\frac{4}{3}\pi k_f^3$ states. So total no. of states is twice of $\frac{V}{(2\pi)^3}\cdot\frac{4}{3}\pi k_f^3$ due to spin of electrons.

At $T=0$, all the states within fermi sphere are filled. So Total number of particles

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

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

$\therefore$ de-Broglie wavelength λ_F corresponding to Fermi momentum

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

Fermi energy at 0 K

$$E_F(0) = \frac{\hbar^2}{2m} K_f^2 = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Fermi energy can also be calculated at 0 K as

$$N = \sum_i n_i$$

$$= \int_0^{E_F} g(\epsilon)\, f(\epsilon)\, d\epsilon = \int_0^{E_F} g(\epsilon)\, d\epsilon = \int_0^{E_F} \frac{4\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$$

$$N = \frac{8\pi V}{3h^3} \cdot E_F^{3/2}(0)\,(2m)^{3/2}$$

or, $$\left(\frac{N}{V} 3\pi^2\hbar^3\right)^{2/3} \frac{1}{2m} = E_F(0)$$

or, $$E_F(0) = \frac{\hbar^2}{2m}\left(\frac{N}{V} 3\pi^2\right)^{2/3}$$

The average energy of electrons at absolute zero is

$$\bar{E} = \frac{\int_0^{E_F} \epsilon\, g(\epsilon)\, d\epsilon}{\int_0^{E_F} g(\epsilon)\, d\epsilon}$$

$$= \frac{3}{5} E_F(0)$$

Total energy of the system

$$U = N\bar{E}$$

$$= \frac{3}{5} N E_F(0)$$

The pressure of electrons

$$P = \frac{2}{3}\frac{U}{V} = \frac{2}{5}\frac{N}{V} E_F(0)$$

As temperature increases from 0 K, each free electron of the system does not take energy KT because most of the available states are already filled below $E_F(0)$. Only a small fraction near $E_F(0)$ can be excited to the empty state lying in the range KT about $E_F(0)$. The number of excited

$$N_{ex} = g\{E_F(0)\} \cdot \Delta E \qquad g(E) = \frac{dN}{dE}$$

$$= \frac{3}{2}\frac{N}{E_F(0)} \cdot KT$$

$$= \frac{3}{2} N \frac{KT}{E_F(0)}$$

$$= \frac{3}{2} N \left(\frac{T}{T_F}\right)$$

So only a small fraction $\sim \frac{3}{2}\left(\frac{T}{T_F}\right)$ of the conduction electrons are excited. The total electronic energy

$$U(T) \simeq N_{ex} \cdot KT$$

$$= \frac{3}{2} N K \frac{T^2}{T_F}$$

So the electronic heat Capacity

$$C_v(T) = \frac{\partial U}{\partial T} = 3NK\left(\frac{T}{T_F}\right)$$

So At room temperature the electronic heat Capacity per electron is $3K\left(\frac{T}{T_F}\right)$ is very small compared to the atomic heat capacity which is about $3K$ per atom.

We Can write down the electronic heat Capacity as

$$C_v^e(T) = \gamma T \quad \text{where } \gamma \text{ is a Constant.}$$

The atomic heat Capacity i.e because of the lattice vibration is proportional to T^3 at low temperatures so the total heat Capacity of metals at low temperature Can be written as

$$C_v = C_v^e + C_v^L$$

or, $$C_v = \gamma T + AT^3 \Rightarrow \frac{C_v}{T} = \gamma + AT^2$$

In the plot of $\frac{C_V}{T}$ with T^2, a straight line is obtained whose intercept on the vertical axis gives the value of coefficient γ.

When temperature is raised above $T = 0$, then the chemical potential is given by

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

i.e

$$N = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \epsilon^{1/2} f(\epsilon)\, d\epsilon$$

$$= \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2 + \cdots\right]$$

Total energy when $T << T_F$

$$U = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \epsilon \times \epsilon^{1/2} f(\epsilon)\, d\epsilon$$

$$\simeq \frac{V}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[\mu(T)\right]^{5/2}\left[1 + \frac{5\pi^2}{8}\left\{\frac{kT}{E_F(0)}\right\}^2 + \cdots\right]$$

$$U = \frac{3}{5} N \mu(0) \left[1 + \frac{5\pi^2}{12} \left(\frac{KT}{E_F(0)} \right)^2 + \cdots \right]$$

Therefore, specific heat a constant volume

$$C_v = \frac{\pi^2}{2} N K \left(\frac{T}{T_F} \right)$$

So specific heat of free electron gas in metal is proportional to the absolute temperature.

$$C_v^e \propto T.$$

According to Debye theory,

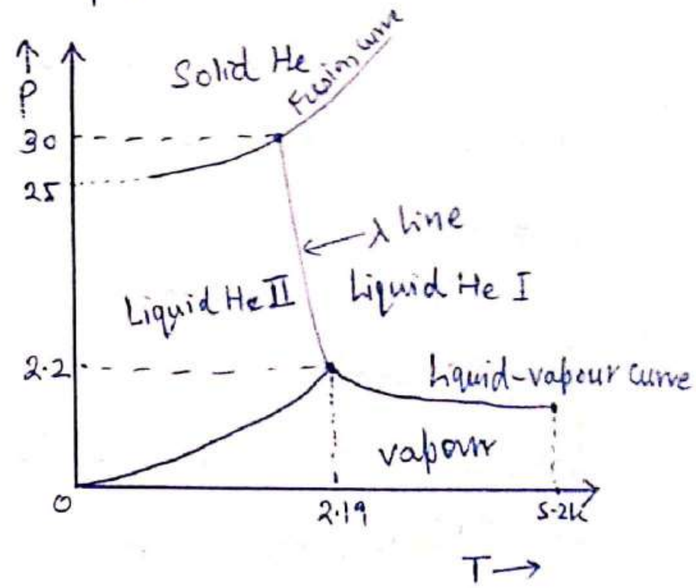
$$C_v^L = 3NK \left[1 - \frac{1}{20} \left(\frac{\theta_D}{T} \right)^2 + \cdots \right] \quad \text{for } \theta_D \ll T$$

$$= \frac{12\pi^4}{5} NK \left(\frac{T}{\theta_D} \right)^3 \quad \text{for } T \ll \theta_D$$

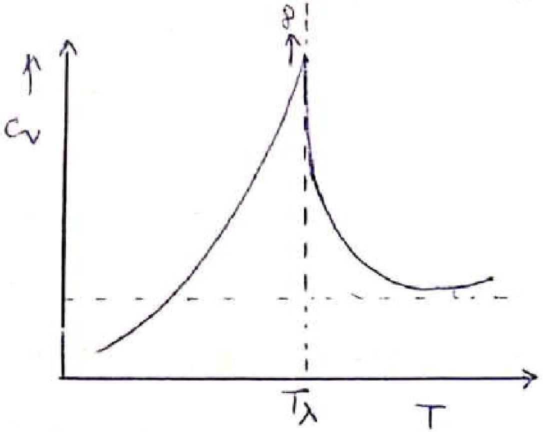
At ordinary temperatures specific heat of free electrons is negligible in comparison to specific heat of lattice. But at low temperatures where T^3 law is valid, contribution of free electrons is observable.

Liquid Helium

A $^4He_2$ atom contains 2 protons, 2 neutrons and 2 electrons i.e even number of fermions. So $^4He_2$ obeys B-E statistics. Liquid helium is colourless, transparent and most volalite liquid. Its boiling point is 4.2 K at 1 atmospheric pressure. It does not changes to solid at any temperature by decreasing its temperature at normal pressure. But it can be converted to solid by applying pressure while cooling. It has no triple point in its phase diagram as all the three phases solid, liquid and vapour do not exist simultaneously. The fusion curve gives the variation of melting point with pressure. At low temperature, fusion curve becomes flat. Therefore even at absolute zero, $^4He_2$ does not change to solid unless pressure on it exceeds 25 atmosphere.



When $^4He_2$ in contact of its vapour is cooled, it begins to show dramatic change in properties at $T = 2.18\ K$. The point $T = T_\lambda = 2.18K$ is called as Lambda point or λ-point.



For $T > T_\lambda$ the behaviour of liquid He is normal and is called He I and for $T < T_\lambda$, liquid He shows remarkable properties such as zero viscosity or superfluidity, zero entropy so liquid He is called He II.

Therefore there is a phase transition occuring in liquid phase called as Lambda transition or λ-transition which devides liquid state into two phases He I and He II.

The specific heat becomes infinite at λ-transition temperature. The variation of specific heat with temperature looks like Greek letter λ therefore transition is called as λ-transition. The temperature $T = T_\lambda = 2.18\ K$ at which

specific heat changes abruptly is called the λ-point.
There is no heat is evolved or absorbed during λ-transi-tion from He II to He I or He I to He II. So no latent heat is involved. It suggests that entropy is continuous across T_λ and there is no change of density at T_λ.
viscosity of He I decreases with decrease in temperature ($T > T_\lambda$). whereas viscosity of He II ($T < T_\lambda$) rapidly decreases with decrease in temperature below T_λ.

London suggests that the λ-transition of $^4He_2$ is a form of Bose-Einstein condensation. if liquid helium is considered as ideal Bose gas.

The transport properties of liquid helium in normal state are not very different from that of normal classical gas. For He I, the ratio of thermal conductivity K to product of coefficient of viscosity and specific heat

$$\frac{K}{\eta C_v} = \begin{cases} 2.6 & \text{at } 2.8\,K \\ 3.2 & \text{at } 4.0\,K \end{cases}$$

The thermal conductivity of He II is abnormally very high, its internal friction is practically zero. When it is force to pass through capillary, the emerging liquid cools while that which remains behind warms up. The densities of He I and He II are ~ $0.1262\ g\,cm^{-3}$ which is less than any other liquid.

The anomalous behaviour of He II ($T < T_\lambda$) could be explained on the basis of two fluid model. He II below T_λ can be considered as consisting of two independent particles, normal particles or fluid (N_n) and superfluids (N_s).

Total no. of particles $N = N_n + N_s$ $\quad T < T_\lambda$

Superfluid has zero entropy and vanishing viscosity. normal fluid ($\epsilon > 0$, for all N_n atoms) contribute to free energy and viscosity.

Mean density $\rho = \rho_n + \rho_s$

Mass velocity u, $\rho u = \rho_s u_s + \rho_n u_n$

Strange properties of He II could be explained on the basis of this model.

References:

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Thank You

For any questions/doubts/suggestions and submission of assignments

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