Phys 570

Physics & Astronomy Dept.
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Lecture #3

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FREE ELECTRON GAS IN THREE DIMENSIONS – Fermi Sphere

The number of orbitals per unit energy range: D(ϵ) = density of states.

$$N = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2} \qquad (19)$$

This leads to:

$$D(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{V}{2\pi^2}.\left(\frac{2m}{\hbar^2}\right)^{3/2}.\varepsilon^{1/2} \qquad (20)$$

Equation (19):

$$\ln N = \frac{3}{2}\ln\varepsilon + const.$$

Hence:

$$\frac{dN}{N} = \frac{3}{2}.\frac{d\varepsilon}{\varepsilon} \Rightarrow D(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{3N}{2\varepsilon} \qquad (21)$$

Within a factor of the order of unity, the number of orbitals per unit energy range at the Fermi energy is the total number of conduction electrons divided by the Fermi energy.

HEAT CAPACITY OF THE ELECTRON GAS

The question that caused the greatest difficulty in the early development of the electron theory of metals concerns the heat capacity of the conduction electrons. *Classical statistical mechanics predicts that a free particle should have a heat capacity of ⅔k_B* where k_B *is the Boltzmann constant.*

If N atoms each give one valence electron to the electron gas, and the electrons are freely mobile, then the electronic contribution to the heat capacity should be *⅔Nk_B* , just as for the atoms of a monatomic gas. *But the observed electronic contribution at room temperature is usually less than 0.01 of this value*.

When we heat the specimen from absolute zero, not every electron gains an energy ~k_BT as expected classically, *but only those electrons in orbitals within an energy range k_BT of the Fermi level are excited thermally*

HEAT CAPACITY OF THE ELECTRON GAS

If N is the total number of electrons, only a fraction of the order of *T/T_F can be excited thermally at temperature T.*
Each of these *NT/T_F electrons has a thermal energy of the order of k_BT.* The total electronic thermal kinetic energy *U is of the order of:*

$$U_{el} \approx N \frac{T}{T_F} k_B T \qquad (22)$$

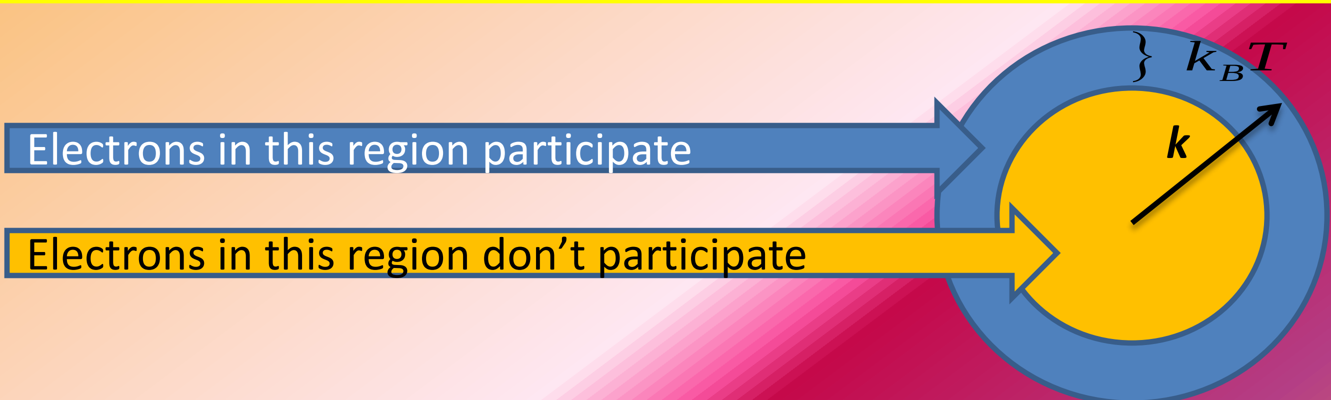
The electronic heat capacity is given by:

$$C_{el} = \frac{\partial U}{\partial T} \approx N k_B \frac{T}{T_F} \qquad (23)$$

C_{el} is directly proportional to *T, in agreement with the experiment*.
At room temperature C_{el} *is smaller* than the classical value *⅔Nk_B by a factor of the order of 0.01 or less, for T_F ~ 5 X 10^4 K.*
Hence: Classical value does not agree with experiment

HEAT CAPACITY OF THE ELECTRON GAS: summary

- Classical Statistical Physics heat capacity of one electron: C= $\frac{2}{3}k_B$
- Classical Statistical Physics heat capacity of N electrons: C = $\frac{2}{3}Nk_B$
- Experimental result of C = 1% of this value only
- Error in Classical theory was due to considering all electrons that participate in conductivity as *Free electrons*.
- Fermi solved this puzzle: Only electrons that have energies of ~ k_BT below Fermi Surface or higher participate in Heat Capacity.
- Hence: only NT/T_F of electrons is important.
- All other electrons are not useful.



HEAT CAPACITY OF THE ELECTRON GAS: summary

- ⇨ *All Free electrons participate in Electrical Conductivity*
- *But only T/T_F fraction participate in Heat Capacity*
- *This conclusion is a major indication of the success of the Fermi Free Electron Gas.*

- We want to derive an expression for the ***electronic heat capacity***:

The increase $\Delta U \equiv U(T) - U(0)$ in the total cnergy of a system of N electrons when heated from 0 to T is:

$$\Delta U \equiv \int_0^{\infty} \varepsilon D(\varepsilon) f(\varepsilon) d\varepsilon - \int_0^{\varepsilon_F} \varepsilon D(\varepsilon) d\varepsilon \qquad (24)$$

Total No of electrons inside Fermi sphere (or including outside where no electros):

$$N = \int_0^{\infty} D(\varepsilon) f(\varepsilon) d\varepsilon = \int_0^{\varepsilon_F} D(\varepsilon) d\varepsilon \qquad (25)$$

we can write (then multply both sides by ε_F:)

$$\int_0^{\infty} d\varepsilon = \int_0^{\varepsilon_F} d\varepsilon + \int_{\varepsilon_F}^{\infty} d\varepsilon$$

$$\left(\int_0^{\varepsilon_F} + \int_{\varepsilon_F}^{\infty} \right) D(\varepsilon) f(\varepsilon) \varepsilon_F d\varepsilon = \int_0^{\varepsilon_F} \varepsilon_F D(\varepsilon) d\varepsilon \qquad (26)$$

Deriving HEAT CAPACITY OF THE ELECTRON GAS

(26) & (24): 6 terms:

$$\Delta U = \int_{\varepsilon_F}^{\infty} (\varepsilon - \varepsilon_F) D(\varepsilon) f(\varepsilon) d\varepsilon + \int_{0}^{\varepsilon_F} (\varepsilon_F - \varepsilon)\left[1 - f(\varepsilon)\right] D(\varepsilon) d\varepsilon \qquad (27)$$

The *first integral* on the right-hand side of (27) gives the energy needed to take electrons from ε_F to the orbitals of energy $\varepsilon > \varepsilon_F$, and the *second integral* gives the energy needed to bring the electrons to ε_F from orbitals below ε_F .

The product *f(ε)D(ε)dε* in the first integral of (27) is the number of electrons elevated to orbitals in the energy range *d*ε at an energy ε. The factor *[1 - f(ε)]* in the second integral is the probability that an electron has been removed from an orbital ε.

The heat capacity is found on differentiating *ΔU* with respect to *T*. The only temperature-dependent term in (27) is *f(ε)*

Deriving HEAT CAPACITY OF THE ELECTRON GAS

The heat capacity of the electron gas is found on differentiating *8U with* respect to *T.*

$$c_{el}=\frac{dU}{dT}=\int_0^\infty d\varepsilon[\varepsilon-\varepsilon_F]\frac{df}{dT}D(\varepsilon) \qquad (28)$$

$$\text{Fermi Dirac: } f(\varepsilon)=\frac{1}{e^{\left(\frac{\varepsilon-\mu}{K_BT}\right)}+1} \qquad (x1)$$

Let $D(\varepsilon)\rightarrow D(\varepsilon_F)$ in (28) and $\mu\rightarrow\varepsilon_F$ in Fermi Dirac Function:

$$\therefore c_{el}\cong D(\varepsilon_F)\int_0^\infty d\varepsilon[\varepsilon-\varepsilon_F]\frac{df}{dT} \qquad (29)$$

equation (x1) becomes:

$$f(\varepsilon)=\frac{1}{e^{\left(\frac{\varepsilon-\varepsilon_F}{K_BT}\right)}+1} \qquad (x2)$$

let $k_B T \rightarrow \tau$:

$$f(\varepsilon) = \frac{1}{e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)} + 1} \qquad (x\,3)$$

we then differentiate w.r.t τ:

$$\frac{df(\varepsilon)}{d\tau} = \frac{\left[-\left(\frac{\varepsilon - \varepsilon_F}{\tau^2}\right) e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)}(-1)\right]}{\left[e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)} + 1\right]^2} = \left(\frac{\varepsilon - \varepsilon_F}{\tau^2}\right) \frac{e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)}}{\left[e^{\left(\frac{\varepsilon - \varepsilon_F}{\tau}\right)} + 1\right]^2} \qquad (x\,4)$$

$$\because \tau = k_B T \Rightarrow d\tau = k_B dT$$

$$\frac{1}{dT} = k_B \frac{1}{d\tau}$$

Rewriting Eq. (29):

$$c_{el} \cong k_B D(\varepsilon_F)\int_0^\infty d\varepsilon[\varepsilon-\varepsilon_F]\left(\frac{\varepsilon-\varepsilon_F}{\tau^2}\right)\frac{e^{\left(\frac{\varepsilon-\varepsilon_F}{\tau}\right)}}{\left[e^{\left(\frac{\varepsilon-\varepsilon_F}{\tau}\right)}+1\right]^2}$$

$$\Rightarrow c_{el} = k_B D(\varepsilon_F)\int_0^\infty d\varepsilon\left(\frac{\varepsilon-\varepsilon_F}{\tau}\right)^2\frac{e^{\left(\frac{\varepsilon-\varepsilon_F}{\tau}\right)}}{\left[e^{\left(\frac{\varepsilon-\varepsilon_F}{\tau}\right)}+1\right]^2} \qquad (30)$$

$$let : x = \left(\frac{\varepsilon-\varepsilon_F}{\tau}\right) \Rightarrow dx = \frac{d\varepsilon}{\tau} = \frac{d\varepsilon}{k_B T} \Rightarrow d\varepsilon = k_B T dx$$

$\rightarrow$ we have $k_B T$ and k_B in (30) $\Rightarrow k_B^2 T$:

Hence, we have:

$$c_{el} = k_B{}^2 T D(\varepsilon_F) \int_{\frac{-\varepsilon_F}{\tau}}^{\infty} dx \;\; x^2 \frac{e^x}{\left[e^x + 1\right]^2} \qquad (31)$$

for the lower limit of integral:

$$x = \left(\frac{\varepsilon - \varepsilon_F}{\tau}\right) \Rightarrow x = \frac{0 - \varepsilon_F}{\tau} = \frac{-\varepsilon_F}{\tau}$$ [lower limit in (30) = ε=0]

as T $\rightarrow$ 0, x $\rightarrow$ -∞

Using table of Integrals:

$$\int_{-\infty}^{\infty} dx \;\; x^2 \frac{e^x}{\left[e^x + 1\right]^2} = \frac{\pi^2}{3} \qquad (32)$$

(32) in (31): $c_{el} = \dfrac{\pi^2}{3} k_B{}^2 T D(\varepsilon_F)$ (33)

From eq. (21) above, we have:

$$D(\varepsilon_F) = \frac{3N}{2\varepsilon_F}$$

$$\therefore D(\varepsilon_F) = \frac{3}{2}\frac{N}{k_B T_F}$$

with: $T_F = \dfrac{\varepsilon_F}{k_B}$, (33) $\rightarrow$:

$$C_{el} = \frac{1}{2}\pi^2 k_B{}^2 \frac{T}{T_F} \qquad (36)$$

$$T_F = Const.$$

Recall that although T_F *is called the Fermi temperature, it is not the electron* temperature, but only a convenient reference notation>
We shall compare this result with experimental data.

Experimental Heat Capacity of Metals:

At temperatures much below both the Debye temperature and the Fermi temperature, the heat capacity of metals may be written as the sum of electron and phonon contributions:

$$C = \gamma T + AT^3$$

where γ and A are constants characteristic of the material.

$\therefore$ Electronic part is Linear to *T*   *(Agree with Fermi Free Electron Model)*

While Phononic part is $\alpha\, T^3$ (Agree with Debye model)