Applications to Quantum Statistics (F-D statistics)

Dr. Neelabh Srivastava
(Assistant Professor)
Department of Physics
Mahatma Gandhi Central University
Motihari-845401, Bihar
E-mail: neelabh@mgcub.ac.in

Programme: M.Sc. Physics
Semester: 2nd

- In this lecture, we will discuss the concept of electron gas in metals and derive the relations for zero point energy, Fermi energy, Fermi pressure and other thermodynamic functions of a completely degenerate and strongly degenerate Fermi-Dirac system.

- We will also see the applications of F-D statistics in explaining the behavior of electronic specific heat capacity and White Dwarf Star.

Fermi energy for electron gas in metals

- Metals are very good conductors and the high conductivity of metals is due to the presence of free electrons. These free electrons move freely within the metal and continuously collide among themselves and also with the fixed ion core. Such behavior of free electrons is similar to that of molecules of a gas. Thus, these free electrons in metals behave like an free electron gas.

- Since, electrons have half-integral spin angular momentum in units of $h/2\pi$, they are Fermions and obey Fermi-Dirac statistics. Such a system of fermions confined in a volume is known as Fermi gas (obeying *Pauli's exclusion principle*).

Difference between Free electron gas and Ordinary gas

Free Electron gas	Ordinary gas
Consists of electrically charged particles	Molecules of an ordinary gas are electrically neutral
Number of electrons per unit volume is greater (10^{29} electrons/m^3)	Number of molecules per unit volume is lesser (10^{25} molecules/m^3)
Obeys Pauli's exclusion principle	Do not obey Pauli's exclusion principle
Free electrons are indistinguishable	Molecules are considered distinguishable
Obeys Fermi-Dirac statistics	Obeys Maxwell-Boltzmann statistics

- Consider an electron gas having ‘n’ free electrons in a conductor whose volume is V. The energy distributed among all the n electrons according to the Fermi-Dirac distribution law is given by –

$$n_i = \frac{g_i}{e^{(\varepsilon_i - \varepsilon_F)/kT} + 1}$$

- If n is very large then spacing between two successive energy levels become very small making almost continuous. Thus, if the electron energy ranges between ε to (ε+dε), number of degenerate states g_i and total number of electrons n_i in these states should be substituted by g(ε)dε and n(ε)dε, respectively.

$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{e^{(\varepsilon_i - \varepsilon_F)/kT} + 1}$$

We know that,

$$g(p)dp = \frac{4\pi V p^2}{h^3} dp$$

Since, electrons have only two allowed values of spin quantum number ($m_s = \pm 1/2$), total number of allowed states in terms of energy is given by -

$$g(\varepsilon)d\varepsilon = \frac{2\times 4\pi V\left(2m\varepsilon\right)}{h^3} d(\sqrt{2m\varepsilon}) = \frac{8\sqrt{2}\pi V}{h^3} m^{3/2}\varepsilon^{1/2} d\varepsilon$$

$$n(\varepsilon)d\varepsilon = \frac{8\sqrt{2}\pi V}{h^3}\frac{m^{3/2}\varepsilon^{1/2}d\varepsilon}{\exp\left(\frac{\varepsilon_i - \varepsilon_F}{kT}\right)+1}$$

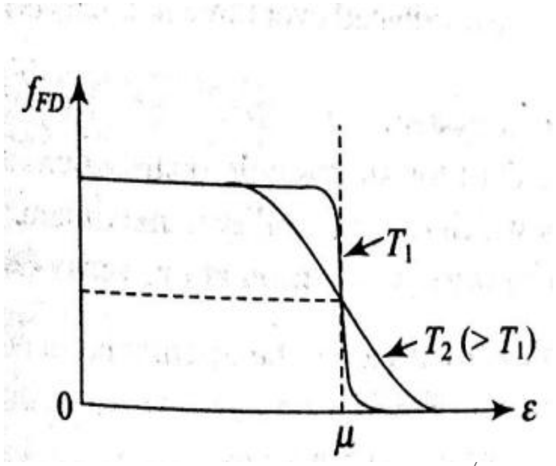
This relation gives the Fermi-Dirac law of distribution of energy among electrons.

Fermi Energy

Now, it is obvious from the figure that at T = 0 K, all the single particle states up to ε_F are filled up.

Therefore,

$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{e^{-\infty}+1} = g(\varepsilon)d\varepsilon \quad (\because e^{-\infty}=0)$$



So, the number of electrons is equal to the total number of energy states occupied by the electrons from zero to ε_F since each energy state can have only one electron.

Thus,

$$N=\int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon=\frac{8\sqrt{2}\pi V}{h^3}m^{3/2}\int_0^{\varepsilon_F}\varepsilon^{1/2}d\varepsilon=\frac{16\sqrt{2}\pi V m^{3/2}\varepsilon_F^{3/2}}{3h^3}$$

giving

$$\varepsilon_F=\frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}=\frac{h^2}{8m}\left(\frac{3n}{\pi}\right)^{2/3} \quad and \quad T_F=\frac{\varepsilon_F}{k}=\frac{h^2}{8mk}\left(\frac{3n}{\pi}\right)^{2/3}$$

The above expression of ***Fermi energy*** of electrons in the metal shows that *Fermi energy is independent of size and volume of the conductor and solely depends on the electron concentration (n=N/V).*

Total energy at T = 0K

(Completely degenerate F-D systems)

Total energy of electrons at absolute zero is given by –

$$U = \int_0^{\varepsilon_F} \varepsilon\, n(\varepsilon) d\varepsilon = \int_0^{\varepsilon_F} \varepsilon\, g(\varepsilon) d\varepsilon$$

$$U = \frac{8\sqrt{2}\pi V}{h^3} m^{3/2} \int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon = \frac{16\sqrt{2}\pi V m^{3/2} \varepsilon_F^{5/2}}{5h^3} = \frac{2}{5} C V \varepsilon_F^{5/2}$$

$$where\ C = \frac{8\sqrt{2}\pi m^{3/2}}{h^3}$$

$$U = \frac{3}{5} N \varepsilon_F$$

This result shows that unlike a classical particle, a fermion has appreciable energy even at absolute zero which is due to quantum effect arisen out of the Pauli principle. This clearly brings out the inadequacy of classical statistics in describing the behavior of a completely degenerate F-D gas.

Since, $$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

so, this implies that the heat capacity of a fermion system drops to zero at absolute zero. Similarly, entropy of a F-D system also vanishes at absolute zero.

Now, the ground state pressure exerted by a fermion system is given by -

$$P_0 = \frac{2U}{3V} = \frac{2N}{5V}\varepsilon_F = \frac{2}{5}n\varepsilon_F = \frac{2}{5}\frac{h^2}{8m}\left(\frac{3}{\pi}\right)^{2/3} n^{5/3} \propto n^{5/3}$$

Strongly degenerate F-D systems ($T<<T_F$)

From FD distribution function, we find that the mean occupation number n(ε) drops to ½ at $\varepsilon=\varepsilon_F$. As the temperature is raised above absolute zero, electrons are excited from single particle states with ε < μ to states with ε > μ which appears in the form of a tail in n(ε) vs ε plot. Moreover, μ depends on temperature.

Now, total number of particles at a finite temperature in terms of $x=\frac{\varepsilon}{kT}$ is given by -

$$N=\frac{8\sqrt{2}\pi V m^{3/2}}{h^3}\int_0^\infty \frac{x^{1/2}dx}{e^{x-x_0}+1} \quad ....(i) \qquad where\ x_0=\frac{\mu}{kT}$$

To evaluate the integral, use Sommerfeld's lemma:

$$\int_0^\infty f(x-x_0)\,x^s\,dx = \frac{x_0^{s+1}}{s+1}\left[1+\frac{\pi^2}{6}\frac{s(s+1)}{x_0^2}+.....\right] \quad ....(ii)$$

We, get

$$\int_0^\infty \frac{x^{1/2}dx}{e^{x-x_0}+1} = \frac{2}{3}x_0^{3/2}\left[1+\frac{\pi^2}{8x_0^2}+....\right]$$

$$= \frac{2}{3}\left(\frac{\mu}{kT}\right)^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2+....\right]$$

From eq^n. (i), we have

$$N = \frac{2}{3}CV\mu^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2+.....\right] \quad ....(iii) \quad where\ C = \frac{8\sqrt{2}\pi m^{3/2}}{h^3}$$

So,

$$\varepsilon_F^{3/2} = \mu^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2+.....\right] \quad ....(iv)$$

$$\frac{\mu}{\varepsilon_F}=\left[1+\frac{\pi^2}{8}\left(\frac{kT}{\mu}\right)^2+....\right]^{-2/3}=1-\frac{\pi^2}{12}\left(\frac{kT}{\mu}\right)^2+.... \quad ....(v)$$

Taking into consideration the first two terms and neglecting higher order terms, we get

$$\mu^2=\varepsilon_F^2\left[1-\frac{\pi^2}{6}\left(\frac{kT}{\mu}\right)^2\right]$$

$$\Rightarrow \quad \frac{1}{\mu^2}=\frac{1}{\varepsilon_F^2}\left[1+\frac{\pi^2}{6}\left(\frac{kT}{\varepsilon_F}\right)^2\right] \quad ....(vi)$$

(put $\mu=\varepsilon_F$)

Substituting the value of μ from (vi) into (v), we find

$$\mu = \varepsilon_F \left[1 - \frac{1}{12} (\pi kT)^2 . \frac{1}{\varepsilon_F^2} \left\{ 1 + \frac{1}{6} \left(\frac{\pi kT}{\varepsilon_F^2} \right)^2 \right\} + ... \right]$$

again neglecting higher order terms, we get

$$\mu = \varepsilon_F \left[1 - \frac{1}{12} \left(\frac{\pi kT}{\varepsilon_F} \right)^2 - ..... \right] = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 - ..... \right] \quad ......(vii)$$

At T=0K, this equation reduces to $\mu=\varepsilon_F$. However, as temperature increases, chemical potential lowers somewhat.

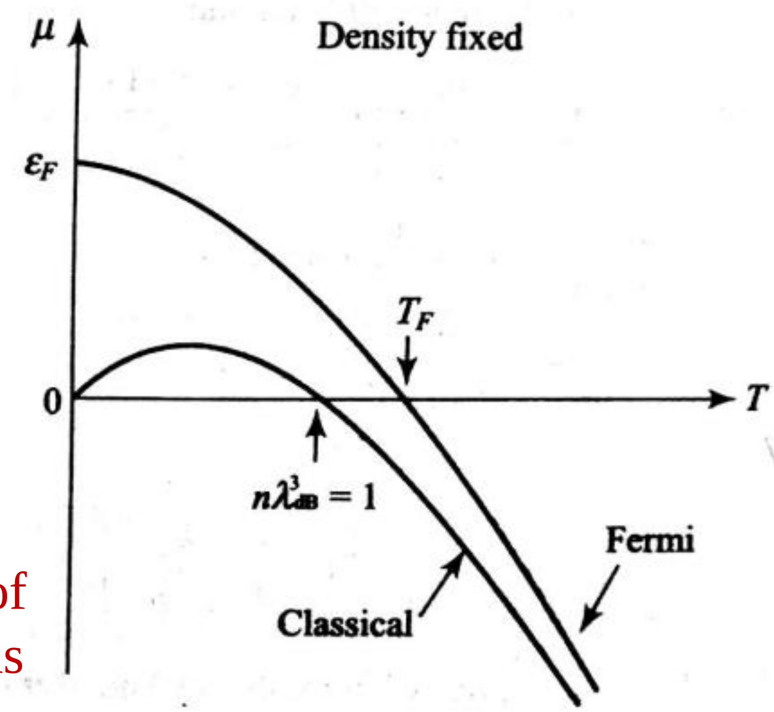


Fig.: Temperature variation of chemical potential of a Fermi gas

Now, to find an expression for the variation of electronic heat capacity with temperature, we will first calculate the internal energy of electrons which is given by –

$$U = \int_0^\infty \varepsilon\, n(\varepsilon) d\varepsilon = CV\left(kT\right)^{5/2} \int_0^\infty \frac{x^{3/2} dx}{e^{x-x_0}+1} \quad ....(viii)$$

$$where \quad x = \frac{\varepsilon}{kT} \; and \; x_0 = \frac{\mu}{kT}$$

again, using Sommerfeld's lemma as previous to evaluate the integral and we get,

$$U = \frac{2}{5} CV\mu^{5/2}\left[1+\frac{5\pi^2}{8}\left(\frac{T}{T_F}\right)^2+.....\right] \quad ....(ix)$$

where we put, $\mu=\varepsilon_F$ in the second term of R.H.S of above expression

From eq^n. (vii) and (ix), we obtain

$$U=\frac{2}{5}CV\varepsilon_F{}^{5/2}\left[1-\frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2+.....\right]^{5/2}\left[1+\frac{5\pi^2}{8}\left(\frac{T}{T_F}\right)^2+.....\right]$$

Using binomial expansion up to the order of $(T/T_F)^2$, we get

$$U=\frac{2}{5}CV\varepsilon_F{}^{5/2}\left[1-\frac{5\pi^2}{24}\left(\frac{T}{T_F}\right)^2+.....\right]\left[1+\frac{5\pi^2}{8}\left(\frac{T}{T_F}\right)^2+.....\right]$$

$$U=\frac{2}{5}CV\varepsilon_F{}^{5/2}\left[1+\frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2-\frac{\pi^4}{16}\left(\frac{T}{T_F}\right)^4+.........\right]\quad ....(x)$$

We can express the total internal energy of a strongly degenerate fermion system ($T << T_F$) in terms of the total zero point energy (of a completely degenerate system) as-

$$E(or\,U) = \frac{3}{5} N\varepsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 - \frac{\pi^4}{16}\left(\frac{T}{T_F}\right)^4 + ... \right] \quad ....(xi)$$

- The above eq^n. shows that the total internal energy of a fermion system increases with temperature.

- For a given values of V, T and N, the energy of an ideal fermion gas is greater than that of a classical gas for $T < T_F$. However, for $T >> T_F$, the energy of a fermion gas approaches the classical value ($\frac{3}{2}NkT$).

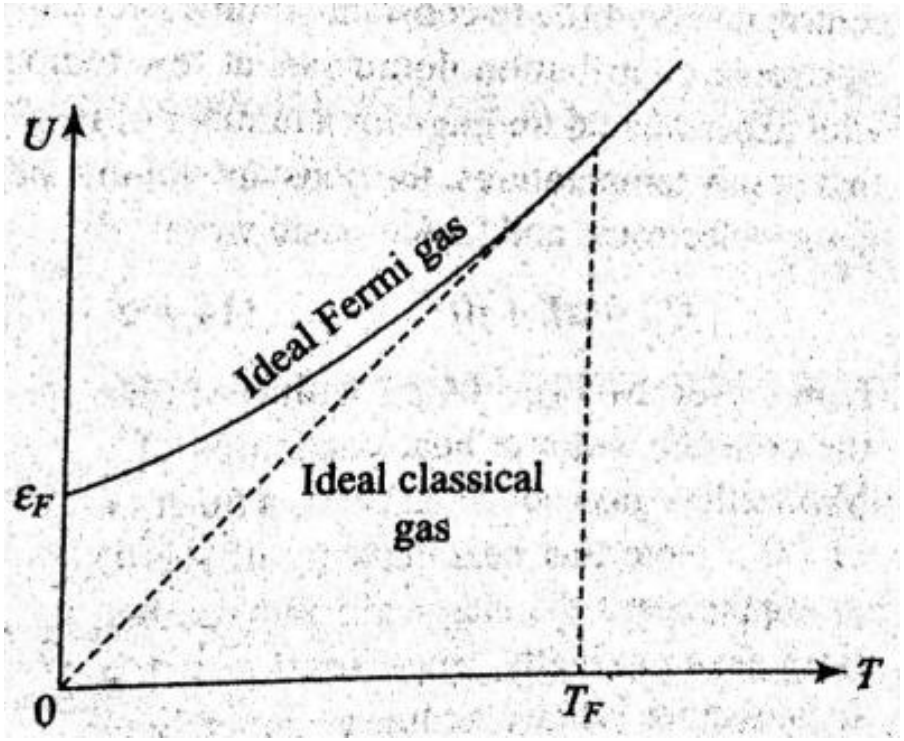


Fig.: Variation of internal energy of a strongly degenerate Fermi gas as a function of temperature

Thermodynamic Functions of Degenerate F-D gas

- **Thermal capacity (C_V):**

$$\because \quad C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{\partial}{\partial T}\left[\frac{3}{5}N\varepsilon_F\left\{1+\frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2+\ldots\right\}\right]_v$$

$$C_v = \frac{\pi^2 N\varepsilon_F}{2}\left(\frac{T}{T_F^2}\right) = \frac{\pi^2}{2}\left(\frac{Nk}{T_F}\right)T = \frac{\pi^2}{2}\left(\frac{kT}{\varepsilon_F}\right)R \quad \ldots\ldots\ldots(xii)$$

Again, if we use eq^n. (xi) for the terms up to $(T/T_F)^4$ then eq^n. (xii) modifies to

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{\pi^2}{2}\left(\frac{Nk}{T_F}\right)T\left[1-\frac{3\pi^2}{10}\left(\frac{T}{T_F}\right)^2+\ldots.\right] \ldots\ldots\ldots(xiii)$$

Thus $\quad C_v \to 0 \quad as \quad T \to 0$

- From experimental results, it has been found that at ordinary temperatures, the contribution to the specific heat of metals due to electrons would be negligible as compared to the contribution due to the atoms. However, electronic contribution dominates at low temperatures.

- At low temperature, the constant volume heat capacity of a metal is made up of two parts – *electronic* and *lattice* as

$$C_v = \alpha T + \beta T^3 \quad \text{..........}(xiv)$$

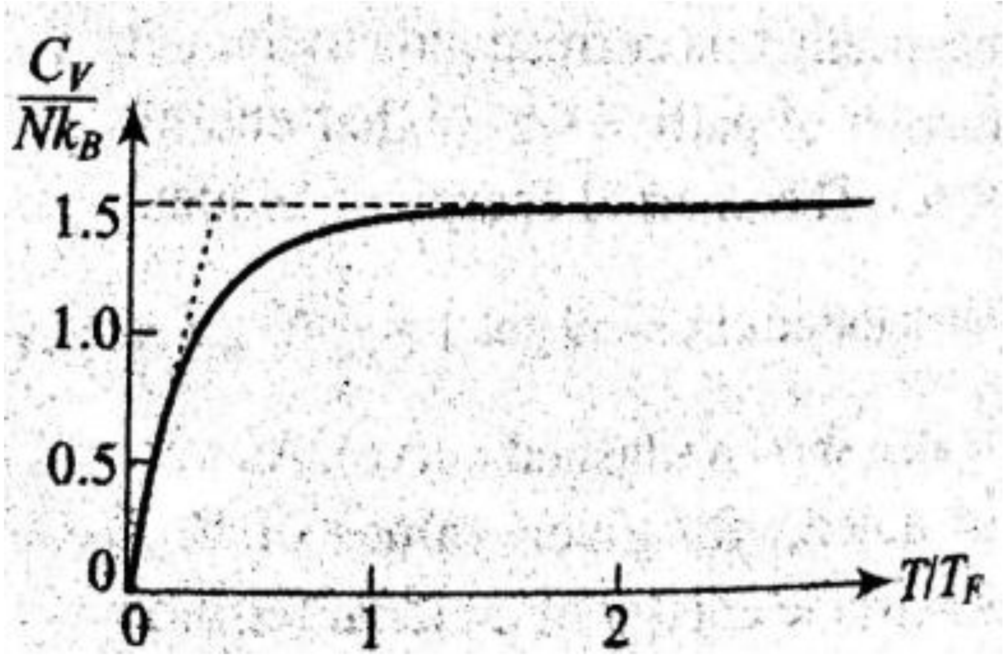


Fig.: Variation of constant volume heat capacity of an ideal Fermi gas with temperature

- **Entropy (S) :**

$$S = \int_0^T \frac{C_v}{T} dT = \int_0^T \frac{\pi^2}{2}\left(\frac{Nk}{T_F}\right) T \frac{dT}{T} = \frac{\pi^2}{2}\left(\frac{Nk}{T_F}\right) T \quad ....(xv)$$

➢ This shows that as $S \to 0$, $T \to 0$ i.e. entropy of a strongly degenerate F-D gas drops to zero at absolute zero temperature. This is in consistent to Third law of thermodynamics.

If we use eq^n. (xiii), then

$$S = \frac{\pi^2}{2}\left(\frac{Nk}{T_F}\right) T \left[1 - \frac{\pi^2}{10}\left(\frac{T}{T_F}\right)^2 + ...\right] ....(xvi)$$

- **Helmholtz Free Energy (F) :**

Since, F=U-TS

Putting the values of U and S from eq^n. (xi) and eq^n. (xvi), we get

$$F = \frac{3}{5} N\varepsilon_F \left[1 - \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + ... \right] ....(xvii)$$

- Pressure exerted by a fermion system is given by-

$$P=-\left(\frac{\partial F}{\partial V}\right)_T=\frac{2}{5}\frac{N\varepsilon_F}{V}\left[1+\frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2+....\right]........(xviii)$$

Comparing above eq^n. with eq^n. (xi), we find

$$P=\frac{2E}{3V}......(xix)$$

White Dwarf Stars

- White dwarf stars are relatively old stars, almost in their end phase of their lives. They are small in diameter and very faint but extremely dense. Typical known white dwarfs are – Sirius B, 40 Eridani B, Van Maalu etc. A plot of luminosity of star versus temperature is shown in figure which is known as Hertz-Russel diagram (H-R diagram).

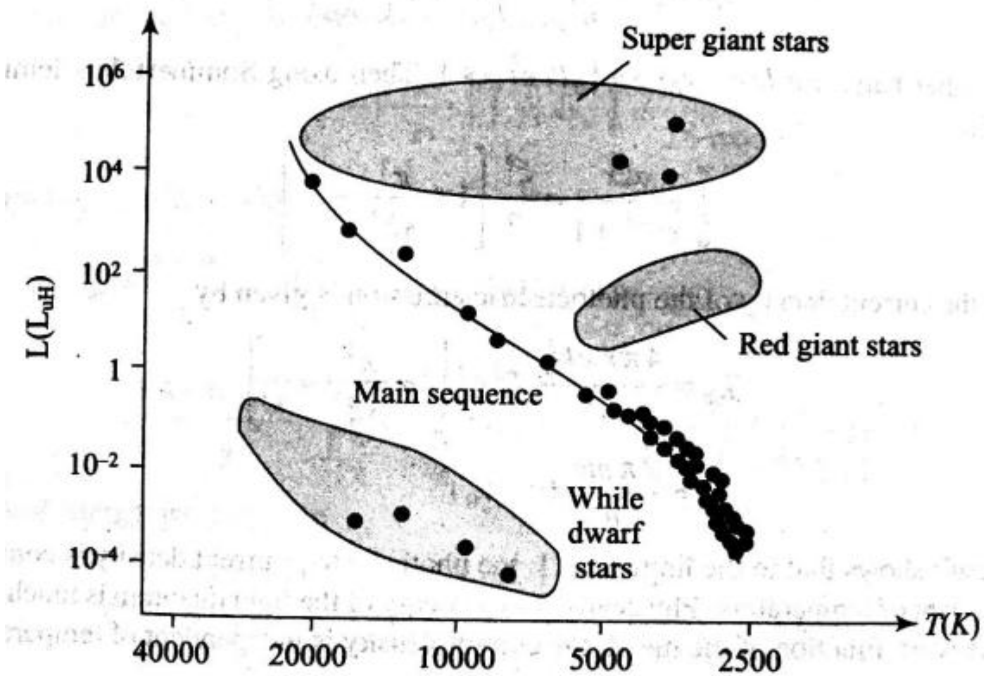


Fig.: location of known white dwarf stars on H-R diagram

- White dwarf are stars which are much fainter, possess small diameter and are very dense compared to other stars of the same mass. Some data are –

Content: mostly Helium

Density: 10^{10} kg/m^3 (10 × density of the Sun)

Mass: mass of helium (~ 10^{30} kg) under extreme pressure

Temperature: 10^7 K (Sun's temperature)

- Thus, white dwarf star is a mass of Helium at an extremely high temperature and under external compression. At this temperature, helium atoms are expected to be completely ionised and the star may be regarded as a gas composed of helium nuclei and electrons.

- The constituents of the star may therefore taken as N electrons (each of mass, m_e) and N/2 helium nuclei (each of mass = $4m_p$). So, mass of the star is given by –

$$M = Nm_e + 4m_p \times N/2 = N(m_e + 2m_p) \approx 2Nm_p \text{......(i)}$$

So, number density of electrons in a typical white dwarf star is –

$$n = \frac{N}{V} = \frac{M/2m_p}{M/\rho} = \frac{\rho}{2m_p} \text{......}(ii)$$

Considering electron density (of Sirius B) is ~ 1.7×10^{36} electrons/m^3 giving rise to Fermi energy of ε_F~0.33MeV and Fermi temperature, $T_F \approx 10^9$ K.

- Since, as we know that rest mass of energy of an electron is 0.5 MeV. Thus, the dynamics of electrons in a typical white dwarf star is *relativistic* can be considered as a highly degenerate electron gas which is uniformly distributed in the star.

- For a relativistic particle, the energy-momentum relation is given by – $\varepsilon = \sqrt{p^2c^2 + m^2c^4}$

- Therefore, the ground state energy of a F-D gas is -

$$E_0 = \frac{2V}{h^3}\int_0^{p_F}\sqrt{p^2c^2 + m^2c^4}\,.4\pi p^2 dp$$

where p_F is the Fermi momentum, defined by –

$$p_F = \left(\frac{3Nh^3}{8\pi V} \right)^{1/3}$$

Thus,

$$E_0 = \frac{4\pi V}{h^3} \int_0^{p_F} mc^2 \left[1 + \left(\frac{p}{mc} \right)^2 \right]^{1/2} p^2 dp$$

substituting, $x_F = \frac{p_F}{mc}$ in above, we get

$$E_0 = \frac{8\pi V m^4 c^5}{h^3} \int_0^{x_F} \left[1 + x^2\right]^{1/2} x^2 dx = \frac{8\pi V m^4 c^5}{h^3} f(x_F)$$

where

$$f(x_F) = \int_0^{x_F} \left[1 + x^2\right]^{1/2} x^2 dx = \begin{cases} = \frac{1}{3} x_F^3 \left(1 + \frac{3}{10} x_F^2 + \ldots \right) & for\ x_F << 1 \\ = \frac{1}{3} x_F^4 \left(1 + \frac{1}{x_F^2} + \ldots \right) & for\ x_F >> 1 \end{cases}$$

The case $x_F << 1$ corresponds to the non-relativistic case, whereas $x_F >> 1$ corresponds to the relativistic case.

Now,

$$x_F = \frac{p_F}{mc} = \frac{h}{mc}\left(\frac{3N}{8\pi V}\right)^{1/3}$$

$$where \quad \frac{N}{V} = \frac{M/2m_p}{\frac{4}{3}\pi R^3} \quad giving \quad x_F = \frac{h}{2\pi Rmc}\left(\frac{9\pi N}{8m_p}\right)^{1/3} = \frac{\overline{M}^{1/3}}{\overline{R}}$$

where $\overline{M} = \frac{9\pi M}{8m_p} \quad and \quad \overline{R} = R\left(\frac{2\pi mc}{h}\right)$ is mass of white dwarf star in terms of proton mass and radius of a white dwarf star in terms of the Compton wavelength of the electron.

Pressure exerted by the Fermi gas is –

$$P_0 = -\frac{\partial E_0}{\partial V} = \begin{cases} \dfrac{8\pi m^4 c^5}{15h^3} x_F^5 & for \quad x_F << 1 \\ \dfrac{2\pi m^4 c^5}{3h^3}\left(x_F^4 - x_F^2\right) & for \quad x_F >> 1 \end{cases}$$

This enormous zero-point pressure exerted by the electron gas in a white dwarf star is counterbalanced by gravitational attraction between helium gas that binds the star.

Utilizing gravitational potential energy concept (for deriving mass-radius relation), it has been found that no white dwarf star can have a mass larger than

$$\mathbf{M_0 = 1.44\Theta}$$

where Θ denotes the mass of Sun (≈ 2×10^{30} kg).

This mass is known as the ***'Chandrasekhar limit'***.

References: Further Readings

1. *Thermal Physics (Kinetic theory, Thermodynamics and Statistical Mechanics)* by S.C. Garg, R.M. Bansal and C.K. Ghosh

2. *Statistical Mechanics* by R.K. Pathria

3. *Statistical Mechanics* by K. Huang

4. *Statistical Mechanics* by B.K. Agrawal and M. Eisner

5. *Elementary Statistical Mechanics* by Gupta & Kumar

Assignment

1. Apply F-D statistics to thermionic emission in metals and hence deduce Richardson-Dushmann equation.

2. Apply F-D statistics to photoelectric emission phenomenon and explain the results.

Thank You

For any questions/doubts/suggestions and submission of assignment

write at E-mail: neelabh@mgcub.ac.in