CHAPTER II

THOMAS-FERMI MODEL

An application of the Fermi statistics was made by Thomas (1927) and Fermi (1928) for calculating the charge distribution and the electric field in the extra-nuclear space of a heavy atom. Their approach was based on the observation that the electrons in this system may be regarded as a completely degenerate Fermi gas of non-uniform distribution, $n(r)$.

By considering the equilibrium state of the configuration, one arrives at a differential equation whose solution gives directly the electric potential $\phi(r)$ and the electron distribution $n(r)$ at point $\vec{r}$. By the very nature of the model, this is generally referred to as the *Thomas–Fermi model* of the atom.

According to the statistics of a completely degenerate Fermi gas, we have exactly two electrons (with opposite spins) in each elementary cell of the phase space, with $p \leq p_F$; the Fermi momentum p_F of the electron gas is determined by the electron distribution n. First, we start for particulars by Fermi statistics.

Fermi statistics

In this case of Fermi statistics, the quantum grand partition function takes the form

$$\Xi_G(\beta,\lambda) = \sum_{\{n_s\}} e^{-\beta\sum_{s=1}^{\infty} n_s(\varepsilon_s-\mu)} = \prod_{s=1}^{\infty}\left(\sum_{n_s} e^{-\beta n_s(\varepsilon_s-\mu)}\right). \quad (2.1.1)$$

We define $-\lambda = \beta\mu$. Where the sum on the individual n_s is restricted by the Fermion statistics

$$n_s = 0,1 \quad (2.1.2)$$

That is the crucial factoring of the sum in equation (2.1.1) into the product of individual sums. These sums are immediately evaluated with the aid of equation (2.1.2) to yield

$$\Xi_G(\beta,\lambda)=\prod_{s=1}^{\infty}\left[1+e^{-\beta(\varepsilon_s-\mu)}\right]. \tag{2.1.3}$$

Hence, logarithm both side of equation (2.1.3),one finds

$$\ln\Xi_G(\beta,\lambda)=\sum_{s=1}^{\infty}\ln\left[1+e^{-\beta(\varepsilon_s-\mu)}\right]; \tag{2.1.4}$$

and the (mean) number of particles follows

$$\bar{N}=-\left(\frac{\partial\ln\Xi_G}{\partial\lambda}\right)_{\beta,V}=\frac{1}{\beta}\left(\frac{\partial\ln\Xi_G}{\partial\mu}\right)_{\beta,V}. \tag{2.1.5}$$

Substitute (2.1.4) into (2.1.5), direct evaluation yields

$$\bar{N}=\frac{1}{\beta}\sum_{s=1}^{\infty}\frac{\beta e^{-\beta(\varepsilon_s-\mu)}}{1+e^{-\beta(\varepsilon_s-\mu)}}; \tag{2.1.6}$$

which gives

$$\bar{N}=\sum_{s=1}^{\infty}\frac{1}{e^{\beta(\varepsilon_s-\mu)}+1}. \tag{2.1.7}$$

For the mean number of particle in each of the state, we define

$$\bar{n}=n(\varepsilon)\equiv\frac{1}{e^{\beta(\varepsilon_s-\mu)}+1}. \tag{2.1.8}$$

The equation (2.1.8) is called "Fermi-Dirac distribution".

The monatomic ideal gas

Considering a non-interacting quantum gas of fermions periodic boundary conditions in a large box of volume $V = L^3$ as in Figure 1

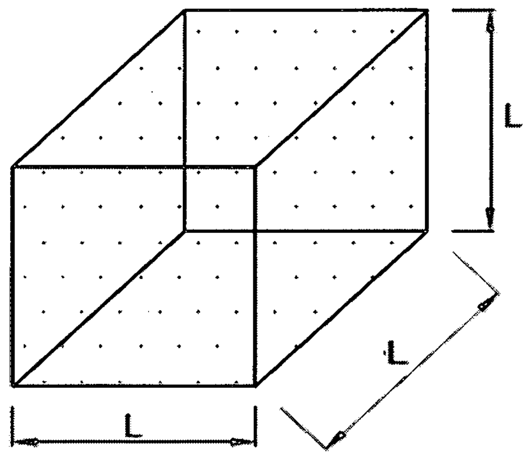

Figure 1 Non-interacting quantum gas of fermions periodic boundary conditions in a large box $V = L^3$

From quantum mechanics of particle in a box, the energy which correspond with each of the permitted principal quantum number may be written as

$$\varepsilon = \frac{\hbar^2 \pi^2 n^2}{2mL^2}; \qquad (2.2.1)$$

where

$n^2 = n_x^2 + n_y^2 + n_z^2 ; n_x, n_y, n_z = 1, 2, 3, \ldots$, these are the principal quantum numbers or the number of state. m is the mass of particle.

The number of states between n and $n + dn$ has been shown in Figure 2

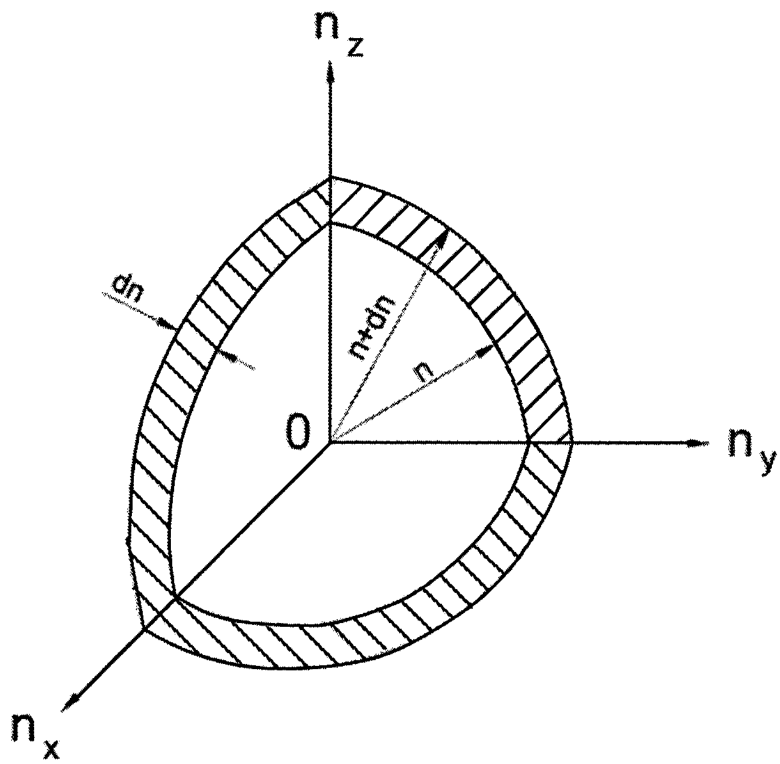

Figure 2 The coordinates in number of state are n_x, n_y, n_z. The number of state available to a particle with a state whose magnitude is between n and $n+dn$ is proportional to the volume of a spherical shell in state space of radius n and thickness dn

The number of state $n \to n+dn$

$$= \text{volume of shell interval radius } n \to n+dn$$

$$= \frac{1}{8} \cdot 4\pi n^2 dn$$

$$= \frac{1}{2} \pi n^2 dn. \qquad (2.2.2)$$

And each state has been divide form to $2s+1$, where S is spin quantum number.

Let $g = 2s+1 \equiv$ spin-degeneracy factor,

the number of orbital interval $n \to n+dn$ is

$$No.\text{ of orbital}\left(n \to n+dn\right) = \frac{1}{2} g\pi n^2 dn. \tag{2.2.3}$$

From (2.2.1), equation(2.2.3) has been evaluated, yielding

$$No.\text{ of orbital}\left(\varepsilon \to \varepsilon + d\varepsilon\right) = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon}\, d\varepsilon \equiv D\left(\varepsilon\right) d\varepsilon. \tag{2.2.4}$$

where $D(\varepsilon)$ is the free-particle density of states.

Consider number of particleswithin the interval energy $\varepsilon \to \varepsilon + d\varepsilon$

$$dN = \left\{D\left(\varepsilon\right) d\varepsilon\right\} n\left(\varepsilon\right).$$

From (2.1.8),(2.2.4), we have

$$dN = \left\{\frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{\varepsilon}\, d\varepsilon\right\}\left(\frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1}\right). \tag{2.2.5}$$

In the limit of large volume, (2.2.5) can be drawn to the form

$$N = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \left(\frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1}\right)\sqrt{\varepsilon}\, d\varepsilon. \tag{2.2.6}$$

Consider at zero temperature, $T = 0$, from equation (2.1.8)

$$n\left(\varepsilon\right) = \frac{1}{e^{\beta(\varepsilon_s - \mu)} + 1} \to 1. \tag{2.2.7}$$

Fermi-Dirac distribution becomeslike a unit step function as shown in Figure 3

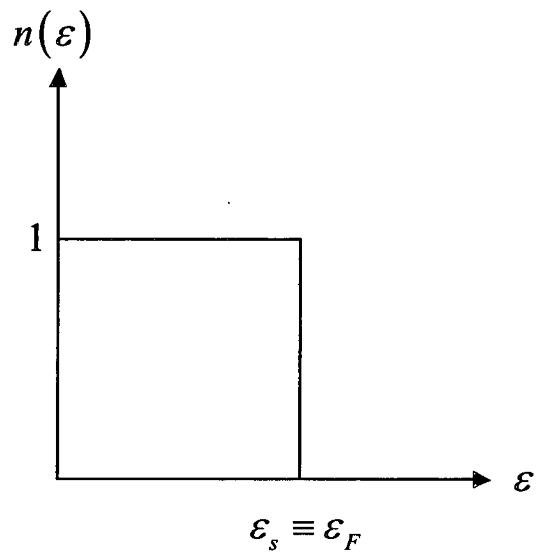

Figure 3 Fermi-Dirac distribution at $T = 0$

For this state, the energy at step function $\varepsilon_s \equiv \varepsilon_F$, where ε_F called the Fermi energy. Hence, equation (2.2.6) can reduce to the form

$$N = \frac{gV}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\infty}\sqrt{\varepsilon}d\varepsilon. \tag{2.2.8}$$

And the Fermi momentum p_F is related to the Fermi energy by

$$\varepsilon_F = \frac{p_F^2}{2m}. \tag{2.2.9}$$

For electrons have spin $s = \frac{1}{2}$, Thus, they have $g = 2$. The number of particles in equation (2.2.8) can be set in the form

$$\frac{N}{V} \equiv n = \frac{1}{\pi^2\hbar^3}\int_0^{p_F} p^2 dp = \frac{p_F^3}{3\pi^2\hbar^3}. \tag{2.2.9}$$

The inversion of this relation expresses the Fermi momentum in terms of the electron distribution

$$p_F = \left(3\pi^2 n\right)^{1/3}\hbar. \tag{2.2.10}$$

Thomas-Fermi equation

According to the formula from (2.2.10), this clearly is a"quasi-classical"description of the situation. Such a description is justifiable if the de Broglie wavelengthof the electrons in a given region of space is much smaller than the distance over which the functions $n(r), p_F(r)$, and $\phi(r)$ fluctuate considerably [2].

Now, the total energy E_{max} of an electron at the top of the Fermi sea at the point $\vec{r}$ is given by [6]

$$E_{max} = T_{Fermi} + U_E(r), \tag{2.3.1}$$

where E_{max} is total energy

T_{Fermi} is kinetic energy from Fermi momentum

$U_E(r)$ is electric potential energy.

Equation (2.3.1) can be rewritten in the form

$$E_{\max} = \frac{p_F^2}{2m} + U_E(r), \tag{2.3.2}$$

with m being the mass of electron.

$E_{\max}$ does not depend on $\vec{r}$ because if this were not the case electrons would migrate to that region of space where $E_{\max}$ is smallest, in order to lower the total energy of the system. The Fermi momentum depends on $\vec{r}$ since $p_F^2/2m = E_{\max} - U_E(r)$.

From equation (2.2.10) and (2.3.2), we have

$$n(r) = \frac{\left(2m/\hbar^2\right)^{3/2}}{3\pi^2}\left[E_{\max} - U_E(r)\right]^{3/2}, \tag{2.3.3}$$

we see that $n(r)$ vanishes when $U_E(r) = E_{\max}$. In the classically forbidden region where $E_{\max} - U_E(r) < 0$ we impose $n(r) = 0$.

Next, the electrostatic potential is definedas

$$\phi(r) = \left(-\frac{E_{\max}}{e}\right) - \left(-\frac{U_E(r)}{e}\right), \tag{2.3.4}$$

where e is electron charge. It follows that $n(r)$ and $\phi(r)$ are related by

$$n(r) = \frac{\left(2m/\hbar^2\right)^{3/2}}{3\pi^2}\left[e\phi(r)\right]^{3/2} \qquad \text{for } \phi(r) \geq 0 \tag{2.3.5}$$

and $n(r) = 0$ for $\phi(r) \leq 0$.

Implement the above relations into the Poisson equation

$$\nabla^2\phi(r) = \frac{e \cdot n(r)}{\varepsilon_0}. \tag{2.3.6}$$

Assuming spherical symmetry, (2.3.6) takes the form

$$\frac{1}{r^2}\frac{d}{dr}\left\{r^2\frac{d}{dr}\phi(r)\right\} = \frac{1}{r}\frac{d^2}{dr^2}\left[r\phi(r)\right] = \frac{e\left(2m/\hbar^2\right)^{3/2}}{3\pi^2\varepsilon_0}\left[e\phi(r)\right]^{3/2} \tag{2.3.7}$$

for $\phi(r) \geq 0$ and

$$\frac{1}{r}\frac{d^2}{dr^2}\left[r\phi(r)\right] = 0$$

for $\phi(r) \leq 0$, with ε_0 being the dielectric constant.

For $r \to 0$ the predominant term of the electrostatic potential is due to the nucleus, it follows that

$$\lim_{r\to 0} r\phi(r) = \frac{Ze}{4\pi\varepsilon_0}, \qquad (2.3.8)$$

where Ze is the charge of the nucleus, and Z is atomic number (for Mercury $Z = 80$). We introduce the dimensionless quantities:

$$r = bx, \qquad r\phi(r) = \frac{Ze}{4\pi\varepsilon_0} y(x),$$

where $b = \left(3\pi^2/2^{7/3}\right) a_0 Z^{-1/3} \approx 0.8853 a_0 Z^{-1/3}$ with $a_0 = \left(4\pi\varepsilon_0\right)\hbar^2 / me^2$ being Bohr radius. The definitions reported above imply the following relation:

$$n(r) = \frac{Ze}{4\pi b^3}\left(y(x)/x\right)^{3/2}, \ y(x) \geq 0 \qquad (2.3.9)$$

with $n(r) = 0, \ y(x) < 0.$

Finally,(2.3.7) can be written in dimensionless formknown as the Thomas–Fermi equation[6]:

$$\frac{d^2}{dx^2} y(x) = \frac{y(x)^{3/2}}{x^{1/2}}, \quad y(x) \geq 0 \qquad (2.3.10)$$

and

$$\frac{d^2}{dx^2} y(x) = 0, \text{for } y(x) < 0.$$

The boundary condition, from equation (2.3.8), for $x = 0$ becomes $y(0) = 1$, And the boundary condition at $r \to \infty$ becomes $\lim_{x\to\infty} y(x) = 0$ [5].

In comparison with electron distribution exact solution [2, 3], in Gaussian units [2] $n(r)$ is written as

$$n(r) = \frac{(2me)^{3/2}}{3\pi^2\hbar^3}\left\{\frac{Ze}{r} y(x)\right\}^{3/2}. \qquad (2.3.11)$$

The solution $y(x)$ will be solved by Modified Adomian Decomposition Method (MADM) incorporated with Padé approximants.