

Quantum Statistical Mechanics

Lecture 6

2-Fermi-Dirac distribution functions

Fermi-Dirac Statistics

Fermi-Dirac Statistics, in quantum mechanics, one of two possible ways in which a system of indistinguishable particles can be distributed among a set of energy states: each of the available discrete states can be occupied by only one particle.

The theory of this statistical behavior was developed (1926–27) by the physicists Enrico Fermi and P.A.M. Dirac, who recognized that a collection of identical and indistinguishable particles can be distributed in this way among a series of discrete (quantized) states.

In contrast to the Bose-Einstein statistics, the Fermi-Dirac statistics apply only to those types of particles that obey Pauli exclusion principle. Such particles have half-integer values of spin and are named fermions, after the statistics that correctly describe their behavior. Fermi-Dirac statistics apply, for example, to electrons, protons, and neutrons.

Fermions obey the Pauli exclusion principle, which forbids more than one particle of this type from occupying a single quantum state.

in quantum mechanics, fundamental mathematical proof that subatomic particles having integral values of spin (such as

photons and helium-4 atoms) must be described by Bose-Einstein statistics , and that subatomic particles having half-integral values of spin (such as electrons and protons) must be described by Fermi-Dirac statistics .

The main application of Fermi–Dirac Statistics is to calculate the properties of electrons.

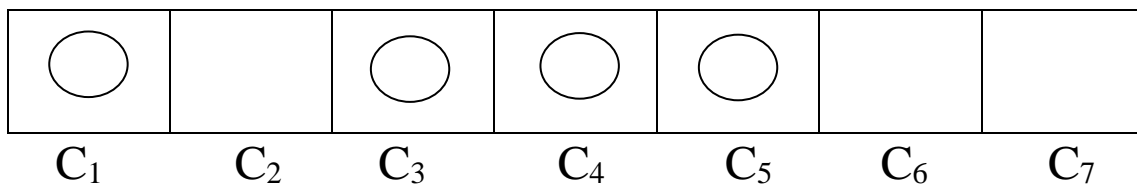
Fermi-Dirac Statistics describes a distribution of particles over energy states in systems of many identical particles that obey the Pauli exclusion principle.

The third statistical model of interest to us assume, as dose Bose-Einstein statistics , that the particles are indistinguishable, but in this case there is a limit of no more than one particle per quantum state. That is,

$N_1 \rightarrow$ Particle in the first energy level E_1

$N_2 \rightarrow$ Particle in the second energy level E_2

In this case, we allow 0 or 1 particle to each quantum state.



Either there is a particle or no particle in each quantum state.

Properties of Fermi-Dirac Statistics:

Accordinging of F.D.S. one conclude that;

- 1- All particles are indistinguishable
- 2- Energy states are distinguishable
- 3- The particles having anti symmetric wave functions are called Fermions (electrons and atoms composed of odd number of fermions obey F.D.S).
- 4- Fermions have half integral angular momentum spin,

$$S = \frac{1}{2}\hbar, \frac{3}{2}\hbar, \frac{5}{2}\hbar, \dots$$

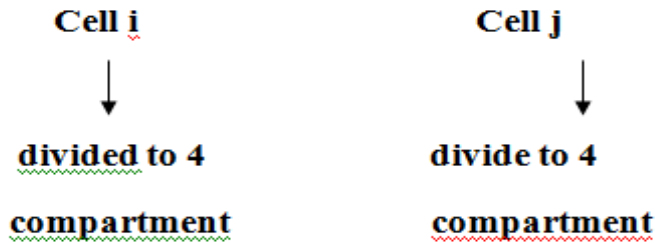
$$\text{Then } S = \left(n + \frac{1}{2}\right)\hbar \quad \text{where } n = 0, 1, 2, 3, \dots$$

- 5- Fermions obey Pauli exclusion principle , (No more than Fermions can be in the same energy state). Or (No two electrons in the same atoms have the same set of quantum number).

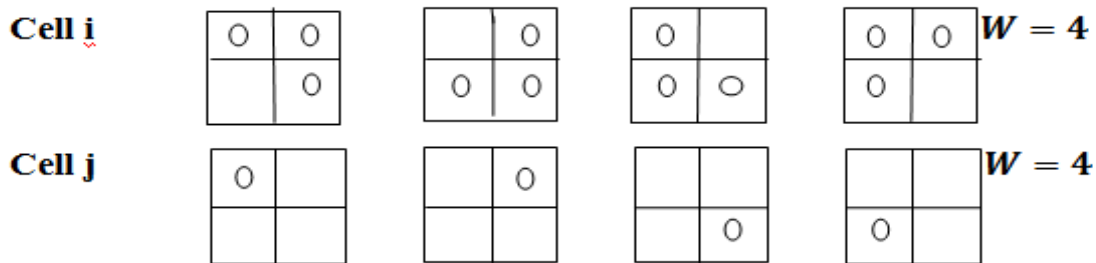
Thermodynamic Probability

Thermodynamic Probability

Let us take a system with just two cell;



Now consider $N_i = 3$, $N_j = 1$



The thermodynamic probability of each cell

$$W_i = 4 \quad \text{and} \quad W_j = 4$$

The total thermodynamic probability of a macrostate is

The thermodynamic probability of each cell

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The total thermodynamic probability of a macrostate is

$$W = W_i \times W_j = 4 \times 4 = 16$$

For B.E.S. \longrightarrow The thermodynamic probability for the same example equal to 80.

In general when there are any number of cells,

$$W = \prod W_i \text{ -----(1)}$$

The thermodynamic probability for a given cell is defined as the number of different ways that the compartments can be divided into just two groups with the occupied compartments in one group and the empty compartments in the other.

Let $N_i \rightarrow$ represent the number of occupied compartments

= The number of phase points in the cell

$n - N_i \rightarrow$ represent the number of empty compartments.

The number of different ways of dividing the compartments into occupied and unoccupied groups. Or

The thermodynamic probability;

$$W_i = \frac{n!}{N_i!(n-N_i)!} \text{ -----(2)}$$

Example;

Let $N_i = 3$ and $n = 4$ (number of compartment) in the i^{th} cell and $N_j = 1$, $n = 4$ in the j^{th} cell. Calculate the thermodynamic probability.

$$W_i = \frac{n!}{N_i!(n-N_i)!} = \frac{4!}{3!(4-3)!} = \frac{1 \times 2 \times 3 \times 4}{1 \times 2 \times 3 \times 1} = 4$$

$$W_j = \frac{n!}{N_j!(n-N_j)!} = \frac{4!}{1!(4-1)!} = \frac{1 \times 2 \times 3 \times 4}{1 \times 1 \times 2 \times 3} = 4$$

Is the same result as before.

Fermi-Dirac distribution functions

The thermodynamic probability for F.D.S. is;

$$W = \prod \frac{n!}{N_i!(n-N_i)!} \text{-----(2)}$$

To maximize subject to the constraints;

$$\sum N_i = N$$

$$\sum \varepsilon_i N_i = U \quad \text{Therefore,}$$

$$\ln W \cong \sum [n \ln n - N_i \ln N_i - (n - N_i) \ln(n - N_i)] \text{---(3)}$$

Where $n \gg N_i \gg 1$

$$\begin{aligned} \partial \ln W &= \sum [-\ln N_i \partial N_i - \partial N_i + \ln(n - N_i) \partial N_i + \partial N_i] \\ &= \sum \ln \left(\frac{n - N_i}{N_i} \right) \partial N_i \\ &= 0 \end{aligned}$$

$$\sum \ln \left(\frac{n - N_i}{N_i} \right) \partial N_i = 0 \text{-----(4)}$$

Now we added in

$$\alpha \sum \partial N_i = 0$$

$$-\beta \sum \varepsilon_i \partial N_i = 0$$

$$\text{So } \sum \left[\ln \left(\frac{n-N_i}{N_i} \right) + \alpha - \beta \varepsilon_i \right] \partial N_i = 0 \text{ -----(5)}$$

$$\text{Or } \ln \left(\frac{n-N_i}{N_i} \right) = -\alpha + \beta \varepsilon_i$$

$$\text{Then, } \frac{n-N_i}{N_i} = e^{-\alpha + \beta \varepsilon_i}$$

Therefore,

$$N_i = \frac{n}{e^{-\alpha} e^{\beta \varepsilon_i} + 1} \text{ -----(6)}$$

$$N_i = \frac{n}{A e^{\beta \varepsilon_i} + 1} \text{ where } A = e^{-\alpha}$$

Which is the Fermi-Dirac Distribution.

Fermi-Dirac distribution function in momentum space

$$\text{As before we define, } \beta = \frac{1}{kT}$$

And in the case of F.D. distribution;

$$n = \frac{2H}{h^3} = \frac{2}{h^3} dx dy dz dp_x dp_y dp_z$$

Here the number 2 is added because there are two independent states of different spin orientation per unit volume in n space.

In this case, the number of phase point $N \rightarrow d^6 N$ and $\varepsilon_i \rightarrow \varepsilon$

Then the F.D. distribution function can be written as;

$$N_i = \frac{n}{e^{-\alpha} e^{\frac{\varepsilon}{kT}} + 1}$$

Or
$$N_i = \frac{n}{\alpha e^{\frac{\epsilon}{kT} + 1}}$$

$$d^6N = \frac{2}{h^3} \frac{1}{\alpha e^{\frac{\epsilon}{kT} + 1}} dx dy dz dp_x dp_y dp_z \text{ -----(7)}$$

Integrating eqn. (7) over all space x, y and z we get;

$$d^3N = \frac{2V}{h^3} \frac{1}{\alpha e^{\frac{\epsilon}{kT} + 1}} dp_x dp_y dp_z \text{ -----(8)}$$

Eqn. (8) represents the F.D. distribution function in three-dimensional momentum space.

If $\alpha e^{\frac{\epsilon}{kT}} \gg 1$ then eqn. (8) becomes;

$$d^3N = \frac{2V}{h^3} \frac{1}{\alpha e^{\frac{\epsilon}{kT}}} dp_x dp_y dp_z \text{ -----(9)}$$

Eqn. (9) is the same as the Maxwell-Boltzmann statistics.

But this approximation can not be made for electron gas, and α must be evaluated from eqn. (8). For this reason the expression for α was first derived by Sommerfeld and is given by.

$$\alpha = e^{-\epsilon_F/kT}$$

Where ϵ_F represent the maximum energy of electrons called the Fermi energy.

According to this approximation eqn. (8) can be written as,

$$d^3N = \frac{2V}{h^3} \frac{1}{e^{-\epsilon_F/kT} e^{\epsilon/kT} + 1} dp_x dp_y dp_z$$

$$d^3N = \frac{2V}{h^3} \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} dp_x dp_y dp_z \text{ -----(10)}$$

$$d^3N = \rho dp_x dp_y dp_z \text{-----}(11)$$

Where $\rho = \frac{2V}{h^3} \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1}$ is the density of the phase points in the momentum space.

Now let $\varepsilon_{F_0} \rightarrow$ represents the energy at $T = 0$

Where $\varepsilon_{F_0} \rightarrow$ is the maximum Fermi energy of the electron at absolute zero. Then the density in terms of ε_{F_0} is;

$$\rho = \frac{2V}{h^3} \frac{1}{e^{(\varepsilon - \varepsilon_{F_0})/kT} + 1} \text{-----}(12)$$

Boundary Conditions

1- if $\varepsilon < \varepsilon_{F_0}$ at $T = 0$ then,

$$\rho_0 = \frac{2V}{h^3} \frac{1}{e^{-\varepsilon_{F_0}/kT} + 1} = \frac{2V}{h^3} \frac{1}{e^{-\infty} + 1}$$

$$e^{-\infty} = 0$$

$$\therefore \rho_0 = \frac{2V}{h^3} \text{-----}(13)$$

This means that at absolute zero the density ρ_0 is constant.

2- if $\varepsilon > \varepsilon_{F_0}$ at $T = 0$ then,

$$\rho_0 = \frac{2V}{h^3} \frac{1}{e^{\varepsilon/kT} + 1} = \frac{2V}{h^3} \frac{1}{e^{+\infty} + 1}$$

$$e^{+\infty} = \infty$$

$$\therefore \rho_0 = 0 \text{-----}(14)$$

Eqn. (14) means that the density of phase points in momentum space is equal to zero where $\varepsilon > \varepsilon_{F_0}$ at $T = 0$.

The Fermi-Dirac Energy Distribution Function

Fermi-Dirac distribution at $T = 0^\circ K$.

Electrons are fermions. Two electrons can occupy a state, one with spin up and one with spin down.

Fermi function $f(\varepsilon)$ is the probability that a state at energy ε is occupied.

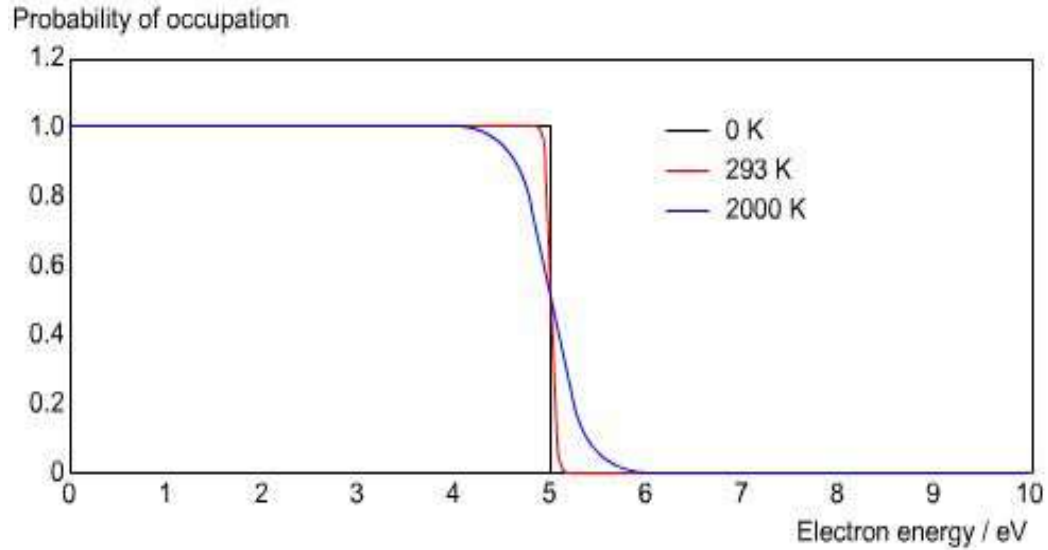
Electrons obey the Fermi-Dirac distribution function

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \varepsilon_F)/kT} + 1} \text{-----(15)}$$

At $T=0^\circ K$, an ideal Fermi gas is in the ground state, and the particles of the gas occupy all quantum states with energy up to a certain maximum value, which depends on the gas density and is called Fermi level (ε_F). Quantum states with energy $\varepsilon > \varepsilon_F$ are empty; such a distribution of occupied and empty states. The distribution function for electrons at $T=0^\circ K$ has the form

$$f(\varepsilon) = \begin{cases} 1, & \varepsilon < \varepsilon_F \\ 0, & \varepsilon > \varepsilon_F \end{cases}$$

That is, all levels below ε_F are completely filled, and all those above ε_F are completely empty.



Fermi-Dirac distribution for several temperatures

The probability that a particle will have energy E

At absolute zero, fermions will fill up all available energy states below a level E_F called the Fermi energy with one (and only one) particle. They are constrained by the Pauli exclusion principle. At higher temperatures, some are elevated to levels above the Fermi level.

$$f(E) = \frac{1}{e^{(E - E_F)/kT} + 1}$$

Fermi-Dirac

See the Maxwell-Boltzmann distribution for a general discussion of the exponential term.

For low temperatures, those energy states below the Fermi energy E_F have a probability of essentially 1, and those above the Fermi energy essentially zero.

The quantum difference which arises from the fact that the particles are indistinguishable.

What happens if the temperature is increased?

Fermi-Dirac distribution at $T > 0^\circ K$

The kinetic energy of the electron gas increase with temperature. Therefore, some energy levels become occupied which were vacant at zero temperature, and some levels become vacant which were occupied at absolute zero.

The distribution of electrons among the levels is usually described by the distribution function $f_{(\varepsilon)}$, which is defined as the probability the level ε is occupied by an electron. Thus if the level is certainly empty, then, $f_{(\varepsilon)} = 0$, while if it is certainly full, then $f_{(\varepsilon)} = 1$. In general, $f_{(\varepsilon)}$ has a value between zero and unity.

Relation between the energy and momentum

The relation between the energy ε and the momentum P is,

$$\varepsilon = \frac{1}{2}mv^2 = \frac{1}{2m}m^2v^2 = \frac{P^2}{2m}$$

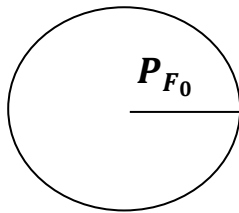
$$\therefore P^2 = 2m\varepsilon$$

For the maximum energy at absolute zero the momentum become maximum,

$$P_{F_0}^2 = 2m\varepsilon_{F_0}$$

$$P_{F_0} = (2m\varepsilon_{F_0})^{1/2} \text{-----(16)}$$

This means that, at absolute zero temperature the momentum space distributed uniformly inside a sphere of radius P_{F_0} and there is no phase point outside the sphere.



Momentum space

The volume of sphere of radius P_{F_0} is equal to

$$\iiint dP_x dP_y dP_z = \frac{4}{3}\pi P_{F_0}^3$$

Now, using equation (11) $d^3N = \rho dp_x dp_y dp_z$ and integrating it over all momentum space

$$N = \rho_0 \iiint dP_x dP_y dP_z \text{-----(17)}$$

At $T = 0^\circ K$, then $\rho_0 = \frac{2V}{h^3}$

Then eqn. 17 becomes

$$N = \frac{2V}{h^3} \times \frac{4}{3} \pi P_{F_0}^3 = \frac{8\pi V}{3h^3} P_{F_0}^3$$

$$\therefore P_{F_0}^3 = \frac{3Nh^3}{8\pi V}$$

$$P_{F_0} = \left(\frac{3Nh^3}{8\pi V}\right)^{1/3} \text{-----(18)}$$

Substituting eqn. 18 in to 16 we obtain

$$\left(\frac{3Nh^3}{8\pi V}\right)^{1/3} = (2m\varepsilon_{F_0})^{1/2}$$

$$2m\varepsilon_{F_0} = \left(\frac{3Nh^3}{8\pi V}\right)^{2/3}$$

$$\varepsilon_{F_0} = \frac{1}{2m} \left(\frac{3Nh^3}{8\pi V}\right)^{2/3}$$

$$\varepsilon_{F_0} = \frac{h^2}{8m} \left(\frac{3N}{\pi V}\right)^{2/3} \text{-----(19)}$$

Which a result in a relationship between the Fermi energy and the number of particles per unit volume.

$h = 6.62 \times 10^{-34} \text{ j. sec}$ Planks constant

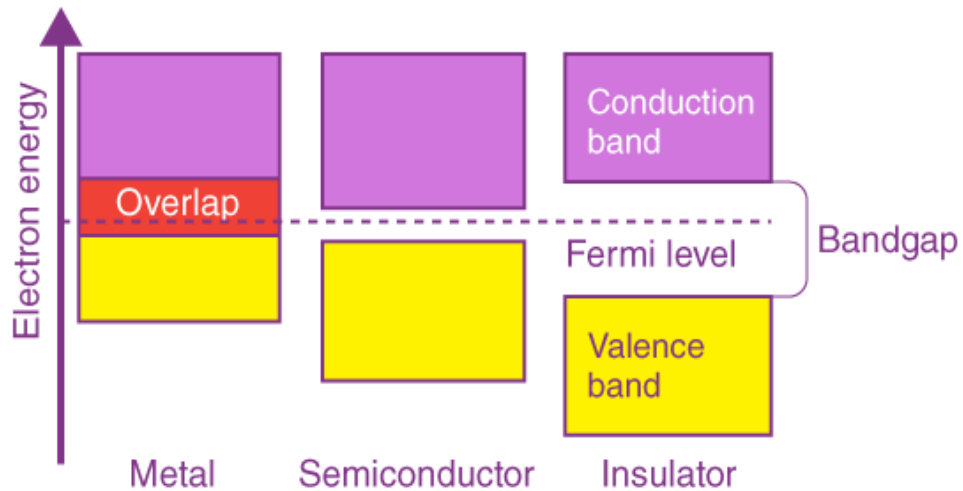
$m = 9.1 \times 10^{-31} \text{ kgm}$ electron mass

$\frac{N}{V}$ number of electron per unit volume

For monatomic $N=1$, diatomic $N=2$

Fermi Energy and Fermi Level

No.	Fermi Energy	Fermi Level
1	Is the energy difference between The highest and lowest occupied Single-particle in a quantum state Of non-interacting fermions at absolute zero T	Is a terms used to describe the collection of electron energy levels at absolute zero T
2	Is defined only at absolute Temperature	Is defined at any temperature
3	Is the kinetic energy difference between highest and lowest occupied single- particle state	Refers to the total kinetic energy and potential energy of a thermodynamic system containing fermions
4	In metals F.E. is the energy difference between F.L. and the lowest occupied single-particle state	Is the energy of the highest occupied single-particle state at zero absolute T
5	Is defined only for non-interacting fermions	Can be defined even for fermions that are in complex interacting systems



Specific heat capacity of the electron gas

The amount of energy needed to raise the temperature of 1kg substance by 1°C is called the **specific heat capacity**. This amount of energy is measured in joules. The Fermi-Dirac statistics attributes a much greater energy to the electron than does the older theory. The change in energy with temperature is very small, and it is only the change in energy that influence the heat capacity.

The average energy $\bar{\epsilon}$ of an electron is defined as;

$$\bar{\epsilon} = \frac{\int_0^{\infty} \epsilon dN_{\epsilon}}{\int_0^{\infty} dN_{\epsilon}} \text{-----} (29)$$

At $T = 0$ and $\epsilon < \epsilon_{F_0}$

Then eqn.28 can be written as;

$$dN_{(\varepsilon)} = \frac{4\pi V}{h^3} (2m)^{3/2} \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\varepsilon_{F_0})/kT} + 1} d\varepsilon \text{ -----(28)}$$

$$dN_{(\varepsilon)} = \frac{4\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2} d\varepsilon \text{ -----(30)}$$

At $T = 0^\circ K$ there are no electron with energies greater than ε_{F_0} , then $\varepsilon < \varepsilon_{F_0}$.

Now substituting eqn. 30 into 29 we obtain

$$\overline{\varepsilon}_0 = \frac{\int_0^{\varepsilon_{F_0}} \frac{4\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2} \varepsilon d\varepsilon}{\int_0^{\varepsilon_{F_0}} \frac{4\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2} d\varepsilon}$$

$$\overline{\varepsilon}_0 = \frac{\int_0^{\varepsilon_{F_0}} \varepsilon^{3/2} d\varepsilon}{\int_0^{\varepsilon_{F_0}} \varepsilon^{1/2} d\varepsilon}$$

$$\overline{\varepsilon}_0 = \frac{\frac{\varepsilon_{F_0}^{5/2}}{5/2}}{\frac{\varepsilon_{F_0}^{3/2}}{3/2}} = \frac{2}{5} \varepsilon_{F_0}^{5/2} \times \frac{3}{2} \varepsilon_{F_0}^{-3/2}$$

$$\overline{\varepsilon}_0 = \frac{3}{5} \varepsilon_{F_0} \text{ -----(31)}$$

The average energy of the electron at $T = 0^\circ K$ is equal to $\frac{3}{5} \varepsilon_{F_0}$ of the maximum energy.

The average energy at any temperature T can be obtained by using the series expansion for ε_F as a function of T .

$$\bar{\varepsilon} = \frac{3}{5} \varepsilon_{F_0} \left[1 + \frac{5\pi^2}{12} \left(\frac{kT}{\varepsilon_{F_0}} \right)^2 + \dots \right] \text{-----(32)}$$

The total energy at constant volume

$$U = N\bar{\varepsilon} \rightarrow dU = Nd\bar{\varepsilon}$$

And the specific heat constant volume is defined as,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = N \frac{d\bar{\varepsilon}}{dT}$$

$$C_V = N \frac{3}{5} \varepsilon_{F_0} \left[\frac{5\pi^2}{12} \times \frac{k^2}{(\varepsilon_{F_0})^2} \times 2T \right]$$

$$C_V = \frac{N\pi^2 k^2}{2\varepsilon_{F_0}} T \text{-----(33)}$$

$N \rightarrow$ Avogadro number

$$Nk = R$$

Then eqn.33 becomes;

$$C_V = \frac{\pi^2 k}{2\varepsilon_{F_0}} RT \text{-----(34)}$$

Eqn.34 shows that the specific heat capacity is dependent on the temperature T according to the Fermi-Dirac statistics, while the Maxwell-Boltzmann statistics predict the specific heat capacity is independent on the temperature $C_V = \frac{3}{2}R$.

The Difference Between Energy Distribution Function For M.B.S, B.E.S And F.D.S

The distribution function $f(E)$ is the probability that a particle is in energy state E . The distribution function is a generalization of the ideas of discrete probability to the case where energy can be treated as a continuous variable. Three distinctly different distribution functions are found in nature. The term A in the denominator of each distribution is a normalization term which may change with temperature.

Maxwell-Boltzmann (classical) $f(E) = \frac{1}{Ae^{E/kT}}$	Bose-Einstein (quantum) $f(E) = \frac{1}{Ae^{E/kT} - 1}$	Fermi-Dirac (quantum) $f(E) = \frac{1}{Ae^{E/kT} + 1}$
Identical but distinguishable particles.	Identical indistinguishable particles with integer spin (bosons).	Identical indistinguishable particles with half-integer spin (fermions).
Molecular Examples: speed distribution	Examples: Thermal radiation Specific heat	Examples: Electrons in a metal Conduction in semiconductor.

Example;

Assume for silver there are one electron per atom, then

$$\frac{N}{V} = 5.86 \times 10^{28} \text{ free electron per m}^3$$

The maximum kinetic energy at absolute zero

$$\begin{aligned}\varepsilon_{F_0} &= \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \\ \varepsilon_{F_0} &= \frac{(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31}} \left(\frac{3}{\pi} \times 5.86 \times 10^{28} \right)^{2/3} \\ &= 9 \times 10^{-19} J = 5.6 eV\end{aligned}$$

This is maximum kinetic energy of electron at absolute zero.

Average energy of electron at absolute zero

$$\bar{\varepsilon} = \left(\frac{3}{5} \right) \varepsilon_{F_0} \text{-----(20)}$$

For silver

$$\bar{\varepsilon} = \left(\frac{3}{5} \right) \times 5.6 \cong 3.46 eV$$

