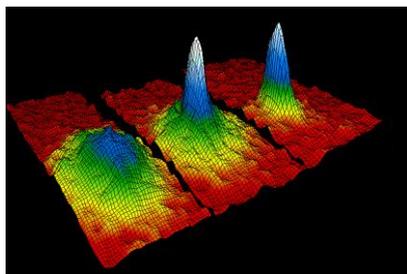A gas of particles with integer spins obeying Bose-Einstein statistics, when cooled to a very low temperature becomes a Bose-Einstein Condensate.

QUANTUM STATISTICS

Structure

STUDY GUIDE

In Unit 13, you have learnt how to evaluate the partition function and thermodynamic functions of a monatomic gas obeying Maxwell-Boltzmann statistics. This exercise required knowledge of elementary differential and integral calculus. However, in this unit, you will apply the basic knowledge of permutations and combinations (Unit 12) to establish distribution functions for Bose-Einstein and Fermi-Dirac systems. You will then study the behaviour of a photon gas using Bose-Einstein statistics. The behaviour of Fermi-Dirac systems at low temperatures will be discussed with particular reference to zero point energy and electronic heat capacity in metals. The mathematics in this unit is somewhat involved and you are advised to refresh your earlier knowledge before starting this unit. Keep pen/pencil with you to solve intermediate steps yourself. Phase out your study and go section by section. Then you will enjoy learning it.

"To see something which nobody else has seen before is thrilling and deeply satisfying. These are the moments when you want to be a scientist."

Wolfgang Ketterle

14.1 INTRODUCTION

In the previous units of this block, you have learnt how to apply statistical methods to study thermodynamic behaviour of systems made up of large number of non-interacting particles. But classical statistics failed to resolve the problem of blackbody radiation.

Also, satisfactory explanation of temperature variation of heat capacity of solids eluded it. Moreover, the concept of zero point energy was completely alien to classical statistics. Similarly, to understand the behaviour of conduction electrons in metals, we have to resort to quantum statistics. Therefore, we begin by discussing need for quantum statistics in Sec. 14.2.

In quantum statistics, we deal with two types of statistics: Bose-Einstein (B-E) statistics and Fermi-Dirac (F-D) statistics depending on the spin of the particles making up the system. Particles with integral spin are called bosons and those with half-integral spins are known as fermions. While fermions obey Pauli Exclusion Principle, no such restriction applies to bosons. Conforming to this condition, we have obtained expressions for distribution functions for B-E and F-D systems in Sec. 14.3 and 14.4, respectively.

You will note that in spite of fundamental difference, the expressions for distribution functions show remarkable similarity. Further, as compared to Maxwell-Boltzmann distribution (Sec. 13.5), the distribution of bosons is skewed towards lower energy states whereas the distribution of fermions is skewed towards higher energy states.

In Sec. 14.6, we have applied B-E statistics to blackbody radiation. We give Bose's derivation of Planck's law, without any reference whatsoever to classical ideas.

In Sec. 14.7, we have discussed applications of F-D statistics. You will learn that an F-D system is quite alive even at absolute zero. We have obtained expression for Fermi energy and given a brief account of temperature variation of heat capacity of metals based on F-D statistics.

Expected Learning Outcomes

After studying this unit, you should be able to:

❖ point out inadequacies of classical statistics and discuss need for quantum statistics;

❖ obtain expressions for the Bose-Einstein and Fermi-Dirac distribution functions;

❖ starting from BE distribution function, obtain expression for Planck's law;

❖ explain the concept of zero point energy; and

❖ obtain an expression for heat capacity of electrons at low temperatures.

14.2 NEED FOR QUANTUM STATISTICS

In classical statistics, we assume that it is possible to simultaneously determine the position and momentum coordinates of a gaseous particle as precisely as we like. It means that these particles are distinguishable and can be labelled. But this is not true in practice. Heisenberg's uncertainty principle forbids determination of the position (q) and the momentum (p) of a particle simultaneously with infinite precision. If the uncertainties in the measurements of q and p are Δq and Δp, respectively, the product $\Delta q \, \Delta p$ cannot be made less than $\hbar / 2$:

$$\Delta q \, \Delta p \geq \hbar / 2 \qquad\qquad\qquad (14.1)$$

where $\hbar = h / 2\pi$ and $h (= 6.62 \times 10^{-34}\,\text{Js})$ is Planck's constant. It implies that when we study the behaviour of an assembly of identical particles statistically, we should treat it as a collection of **indistinguishable** particles. Further, blackbody radiation deserves a unique place in physics because it gave birth to quantum theory. You have learnt about it in detail in Unit 11. But here we will recapitulate some important ideas/results.

14.2.1 Blackbody Radiation

We know that when a body is heated, it emits electromagnetic waves from its surface in all directions. The spectrum of radiated frequencies ranges from 0 to ∞. When such thermal radiation is contained inside a hollow cavity whose walls are opaque to it and maintained at a constant temperature, we expect that in the interior, radiation will have exactly the same spectral distribution as that of blackbody radiation. In other words, the energy distribution over various wavelengths should be a function of temperature, independent of the shape and size of the cavity (Fig. 14.1a). A small opening in one of the walls enables us to experimentally study the nature of emerging radiation. In fact, such experiments were carried out by a large number of scientists in the period of 1895-1900. We may make particular mention of Rubens and Kurlbaum. The results of their experiments established beyond doubt the inability of classical theories to reproduce experimental results. Fig.14.1b shows the experimental curves for the energy density u_λ at three different temperatures.

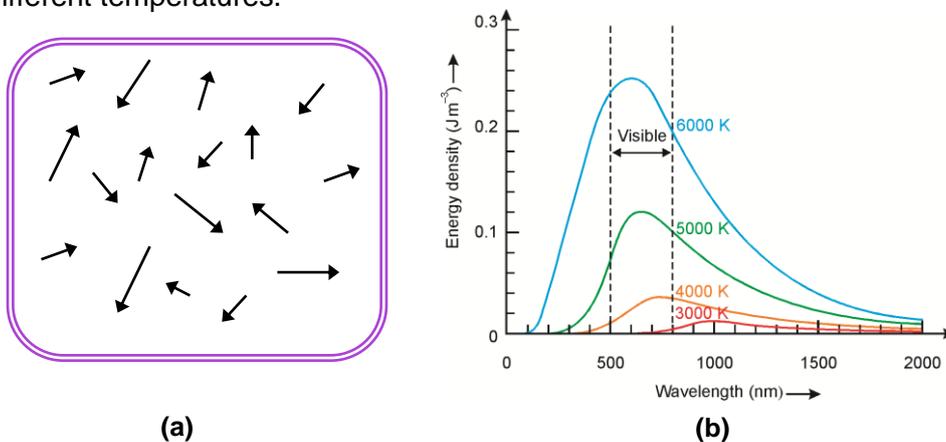| (a) | (b) |

Fig. 14.1: a) The electromagnetic radiation inside an oven is treated as a photon gas in equilibrium with the oven walls; b) Spectral distribution of energy in blackbody radiation.

As discussed in Unit 11, Lord Rayleigh and Sir James Jeans studied the problem using the ideas of classical physics and arrived at **Rayleigh-Jeans law** for $u_\nu d\nu$ [Eq. (11.8)].

You may recall that for small values of ν, it reproduced the experimental curves rather well. However, for $\nu \to \infty$, Rayleigh-Jeans law showed a serious flaw; it predicted that the total energy density would be infinite. This unphysical situation was termed **ultraviolet catastrophe** by P. Ehrenfest (Fig. 14.2).
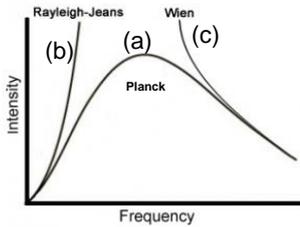
Wien carried out thermodynamic analysis of blackbody radiation spectrum. and successfully explained the qualitative features of experimental results at high frequencies (Fig. 14.2). Though it seemed acceptable, it proved completely inadequate at low frequencies. That is, classical theories failed to explain the observed spectrum of blackbody radiation satisfactorily for all frequencies and serious doubts were expressed about the applicability of the principle of equipartition of energy to blackbody radiation.

Fig. 14.2

At this stage, Max Planck rejected classical theories and conjectured that emission and absorption of radiation are discontinuous processes. On December 14,1900, he declared in a paper presented to the German Physical Society that the only way to derive the correct blackbody radiation formula was to postulate that

- exchange of energy between matter (walls) and radiation (cavity) could take place only in bundles of a certain quantity of energy; and

- the quantum of exchange is directly proportional to its frequency. That is, the energy of an oscillator having frequency ν could only be an integral multiple of $h\nu$, where h is a constant.

Max Karl Ernst Ludwig Planck, (1858 – 1947) was a German theoretical physicist. He is regarded as the originator of the quantum theory which revolutionized our understanding of atomic and subatomic processes. The Nobel Prize in Physics was conferred on him in 1918 for postulating energy quanta, which helped in explaining the black body radiation.
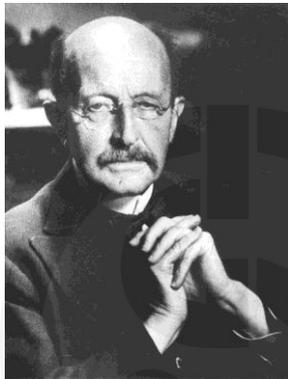
These postulates marked a fundamental departure from then existing ideas. On the basis of his hypothesis that each oscillator can possess only discrete energies; 0, $h\nu$, $2h\nu$,... and oscillators of energy ε_n at a temperature T and by assuming that Maxwell-Boltzmann statistics holds good, Planck arrived at his **law** of blackbody radiation:

$$u_\nu d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{\exp\left(\dfrac{h\nu}{k_B T}\right) - 1}$$

(14.2)

It reproduced experimental curves of Fig.14.1b beautifully. It is pertinent to mention here that Planck's hypothesis of quantisation of energy gave birth to a new branch of physics − Quantum Physics. However, Planck's law is said to be semi-classical. Do you know the reason? It is because he used Rayleigh's results for calculating the number of modes and Maxwell-Boltzmann statistics for distribution of energies.

14.2.2 Heat Capacity of Solids

You have studied that solids behave as a collection of independent harmonic oscillators and energy associated with one mole of a substance is equal to

$3N_A k_B T$, where N_A is Avogadro's number. From the definition of constant volume heat capacity, we can write

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3N_A k_B = 3R = 24.9 \, \text{J} \, \text{mol}^{-1} \text{K}^{-1} \qquad (14.3a)$$

In other words, constant volume heat capacity is constant (= 3R) for all substances and at all temperatures. This is the famous **Dulong and Petit's law**.

Now refer to Fig. 14.3. You will note that experimental data is at complete variance with this law and deviations, particularly in the low temperature region, are very striking.
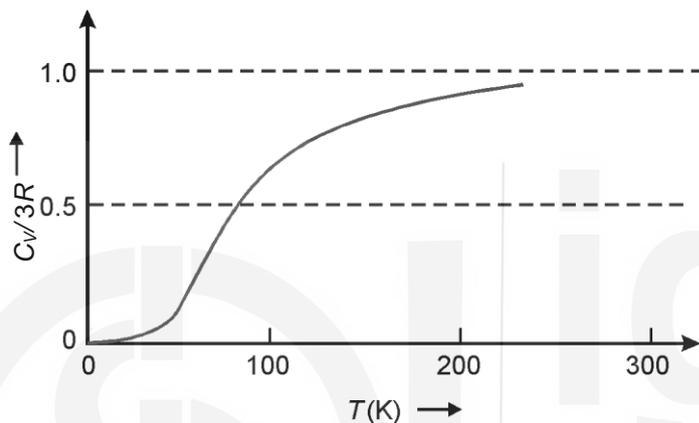

Fig. 14.3: **Temperature variation of constant volume heat capacity of a solid.**

A qualitative theoretical explanation of experimental results was attempted by Einstein using Planck's ideas on quantisation of energy. That is, following Planck, Einstein discarded the law of equipartition of energy. Instead, he assumed that each atom vibrates with the same angular frequency ω_E and the motion of any atom is independent of the motion of its neighbours.

He obtained the following expression for the heat capacity:

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E / T)}{[\exp(\theta_E / T) - 1]^2} \qquad (14.3b)$$

Here ω_E is Einstein's frequency and $\theta_E = \hbar\omega_E / k_B$ is known as Einstein temperature. Einstein could reproduce only the general features of the experimentally observed curve (Fig. 14.4). However, there was disagreement in details, particularly at low temperatures.

Debye (1912) refined Einstein's model and suggested that it would be more appropriate to consider a spectrum of vibration frequencies, particularly at low temperatures. In this way, he showed that at low temperatures, the constant volume heat capacity varies as third power of temperature. This is known as Debye T^3 - law. His results were in excellent agreement with experiments in the entire temperature range.

You may now like to revise important results obtained in this section.

TOWARDS QUANTUM THEORY

- Indistinguishability of particles and uncertainty in the simultaneous determination of position and momentum are basic premises of quantum statistics.

- Spectral distribution of blackbody radiation and temperature dependence of constant volume heat capacity, particularly at low temperatures, cannot be explained on the basis of classical ideas.

- Planck postulated that exchange of energy between matter and radiation takes place only in bundles of a certain quantity of energy and the quantum of exchange is directly proportional to frequency.

- Einstein and Debye used quantisation of vibrational energy to explain the behaviour of heat capacity of solids at low temperatures.

14.2.3 Classification of Particles

You will recall that according to Heisenberg's uncertainty principle, the particles making up a system should not be treated as distinguishable. The detailed consequences of this concept can be understood fully only after a thorough understanding of the principles of quantum mechanics, which you will study in detail in the fifth semester of this programme. For the present, it is sufficient to know that:

a) Simultaneous determination of position and momentum of a particle cannot be accomplished to infinite precision. Instead, uncertainties Δp and Δq in these quantities are subject to $\Delta q \, \Delta p \sim h$. That is, **the volume of a cell in phase space cannot be arbitrarily small**. In fact, the smallest volume of a cell should be taken as h^3.

b) In quantum statistics, identical particles are treated as indistinguishable. It means that permutation of particles does not lead to a different state. This has profound consequences.

c) All known elementary particles can be classified into two categories on the basis of their spin:

   i) Particles having integral spin (0, $\hbar$, 2$\hbar$, …) obey Bose-Einstein statistics and are termed **bosons**. This applies to photons, pions, ^{4}He, etc. The number of bosons that can occupy a given quantum-state has no restriction.

   ii) Particles with half-integral spin $\frac{\hbar}{2}, \frac{3\hbar}{2},...$ are termed **fermions** and obey the Fermi-Dirac statistics. Particles like electrons, protons, neutrons, muons, etc. belong to this category.

Fermions tend to avoid one another!

   The number of fermions in a quantum state is determined by Pauli's Exclusion Principle. For example, there cannot be more than two electrons in the same quantum state having all four quantum numbers the same. You are familiar with the implications of this principle in

electronic configuration of elements in the Periodic Table. In general, the number of fermions in a quantum state is limited to $(2s + 1)$, where $s\hbar$ is the spin angular momentum of the fermion.

You should now test your understanding by answering the following SAQ.

$\mathcal{SAQ}\,1$ – **Classification of particles**

Helium has two isotopes, viz., ^{3}He and ^{4}He. Classify these as fermions and bosons. Justify your conclusion.

To illustrate the consequences of indistinguishability, let us consider the following simple example.

Suppose we have a system consisting of only two particles *A* and *B* and three quantum states, i = 1, 2, 3. According to Maxwell-Boltzmann statistics, these can be distributed in nine ways, which are tabulated below:

Distribution ↓ / States →	1	2	3
1	AB	–	–
2	–	AB	–
3	–	–	AB
4	A	B	–
5	B	A	–
6	A	–	B
7	B	–	A
8	–	A	B
9	–	B	A

That is, we have 3^2 possibilities. It is straightforward to show that if we have N_i particles to be distributed among g_i states, the total number of ways is $g_i^{N_i}$. (It is pertinent to mention here that for convenience, we considered $g_i = 1$ for M-B statistics.)

In the case of quantum statistics, we cannot distinguish *A* from *B*. However, in Bose-Einstein distribution, there is no restriction on the number of particles that can occupy a given state. So, there are only six possibilities:

Distribution ↓ / States →	1	2	3
1	AA	–	–
2	–	AA	–
3	–	–	AA
4	A	A	–
5	A	–	A
6	–	A	A

In general, the result is $^{(N_i+g_i-1)}C_{N_i}$. This can be proved in several ways. We shall do it using a simple, yet interesting method.

Suppose we want to distribute N_i indistinguishable particles among g_i cells. Imagine the N_i – particles, denoted by dots and arranged in a row, as shown in Fig. 14.4a. The cell boundaries are denoted by ($g_i + 1$) vertical bars. For example, when $g_i = 5$ and $N_i = 10$, a typical distribution is shown in Fig. 14.4b.
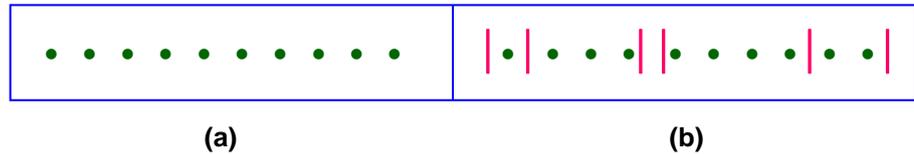

(a)   **(b)**

Fig. 14.4: **a)** N_i **particles arranged along a line; b) a possible distribution for** $N_i = 10$ **and** $g_i = 5$.

There is one particle in the first cell, three in the second, none in the third, four in the fourth, and two in the fifth. The total number of dots and bars is ($g_i + 1 + N_i$). Since the two end positions in such a diagram would always be occupied by bars, the required number of distributions W is equal to the number of ways of choosing N_i positions for the particles from ($N_i + g_i + 1 - 2$), i.e. ($N_i + g_i - 1$) positions. Hence,

$$W = {}^{(N_i+g_i-1)}C_{N_i} \qquad (14.4)$$

If we now put $N_i = 2$ and $g_i = 3$, we get $W = {}^4C_2 = 6$, which reproduces the earlier result.

In the case of Fermi-Dirac statistics, there can, at best, be only one particle per cell and we necessarily have $n_i < g_i$. Of course, for particles of spin $s\hbar$, the number of possibilities has to be multiplied by the factor ($2s + 1$). For the system under consideration, we have just three possibilities as shown below:

Distribution ↓ / States →	1	2	3
1	A	A	–
2	A	–	A
3	–	A	A

If we now define a parameter r as

$$r = \frac{\text{Probability that two particles are found in the same state}}{\text{Probability that the particles are found in different states}}$$

we have $r_{MB} = \dfrac{3/9}{6/9} = \dfrac{1}{2}$, $r_{BE} = \dfrac{3/6}{3/6} = 1$, and $r_{FD} = 0$

These values of r illustrate a striking difference between these three statistics. You should note that $r_{FD} = 0$ because of the Pauli's principle. On the other hand, r_{BE} is greater than r_{MB}. It signifies that bosons have a greater tendency to bunch together; even more than the classical particles.

Before proceeding further, we will like you to know about Prof. S. N. Bose, who is best known for his work on radiation theory.

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Prof. Satyendra Nath Bose (1894-1974) was born on 1st January 1894 in Calcutta (now Kolkata). After matriculation in 1909, he joined Presidency College, Calcutta. He topped his B.Sc. and M. Sc. examinations with specializations in mixed (applied) mathematics. After completing his M.Sc., Bose joined the University of Calcutta, as a research scholar in 1916 and started his studies in the theory of relativity and got interested in the work of Albert Einstein. Since many of his papers were in German, Bose took up to translate them to English for the benefit of all. He was well versed in Bengali, English, French, German and Sanskrit. Apart from science, his interests ranged from poetry to classical music.

In 1924, Bose derived Planck's law of quantum radiation without any reference to classical physics. This was a very fundamental work in the field of quantum statistics. He sent the manuscript of this paper to Einstein, who immediately recognized the importance of his work. Einstein translated this paper in German and sent it for publication to the prestigious *Zeitschrift für Physik* journal on behalf of Bose. Subsequently, Einstein extended the work of Bose to material particles. This led to the birth of Bose-Einstein (B-E) statistics. The particles obeying this statistics are called **bosons**. This name was coined by renowned scientist Paul Dirac to commemorate the great contribution of Bose to the field of quantum statistics.

Bose was nominated National Professor by the Government of India in 1958. In the same year, he was also elected the Fellow of Royal Society.

In 2012, a new particle, popularly known as God particle and responsible for attributing mass to matter, was named Higgs Boson. It was produced in the Large Hadron Collider near Geneva, Switzerland. It is expected to answer how the universe was formed.

We are now equipped with necessary tools to theoretically understand the behavior of quantum particles. The first step in this is to obtain distribution functions for them. You will now learn to obtain expressions for Bose-Einstein distribution function.

14.3 BOSE-EINSTEIN DISTRIBUTION FUNCTION

Consider a system of N non-interacting bosons occupying volume V and sharing energy U. Suppose that the energy levels of the system are very closely spaced so that we can bracket them into groups. We will refer to these as energy cells. This is depicted schematically in Fig. 14.5.

We assume that the number of levels (g_i) in the ith cell is significantly greater than one ($g_i \gg 1$). It is still reasonable to talk about the energy of the levels in the ith cell as ε_i, since they are very close to each other. Let W_i denote the number of ways in which N_i particles can be distributed amongst the g_i levels of the ith cell. This number is available to us from Eq. (14.4).
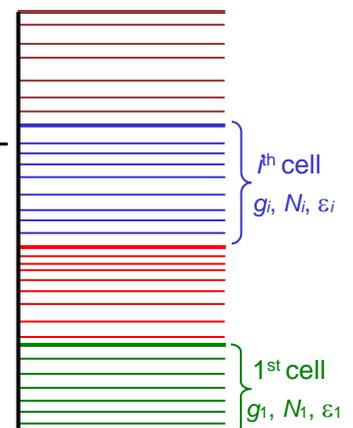

i^{th} cell
g_i, N_i, ε_i

1st cell
g_1, N_1, ε_1

Fig. 14.5: Energy levels of a system bracketed into cells.

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Note that this formalism bears close resemblance to M-B statistics but now we have to deal with identical particles. So, rules for counting the states change. In the instant case, we can write

$$W_i = {}^{(N_i+g_i-1)}C_{N_i} = \frac{(g_i + N_i - 1)!}{N_i!(g_i - 1)!} \qquad (14.5)$$

Recall that the number of ways in which we can put N_1 particles in g_1 levels, N_2 particles in g_2 levels, …, N_i particles in g_i levels defines thermodynamic probability. Let us denote it by $W(N_1, N_2, ..., N_i, ...) = W(\{N\})$. Then we can write

$$W[\{N\}] = \prod_i W_i = \prod_i \frac{(g_i + N_i - 1)!}{N_i!(g_i - 1)!} \qquad (14.6)$$

To obtain the expression for distribution function, we have to maximise W subject to the conditions that total number of particles and total energy of the system are constant:

$$\sum_i N_i = N \qquad (14.7a)$$

and

$$\sum_i N_i \varepsilon_i = U \qquad (14.7b)$$

Following the arguments mentioned in Unit 13, we maximise $\ln W$ rather than W. So, we rewrite Eq. (14.6) as

$$\ln W = \sum_i [\ln(g_i + N_i - 1)! - \ln(g_i - 1)! - \ln N_i!]$$

To extract meaningful information from this expression, we use Stirling's formula and write:

$$\ln W = \sum_i [(g_i + N_i - 1)\ln(g_i + N_i - 1) - (g_i + N_i - 1)$$
$$- (g_i - 1)\ln(g_i - 1) + (g_i - 1) - N_i \ln N_i + N_i]$$

Note that second term on the RHS cancels out with the fourth and sixth terms. On simplification, this expression reduces to

$$\ln W = \sum_i [(g_i + N_i - 1)\ln(g_i + N_i - 1) - (g_i - 1)\ln(g_i - 1) - N_i \ln N_i]$$

Since N_i and g_i are much greater than one, we can ignore one from all the three terms in the RHS of above expression and write

$$\ln W = \sum_i [(g_i + N_i)\ln(g_i + N_i) - g_i \ln g_i - N_i \ln N_i] \qquad (14.8)$$

To maximise $\ln W$, we put $\delta(\ln W) = 0$. Note that g_i is a constant. On using this condition, Eq. (14.8) takes the form

$$\delta \ln W = \sum_i \left[(g_i + N_i)\frac{1}{(g_i + N_i)}\delta N_i + \ln(g_i + N_i)\delta N_i - N_i \frac{1}{N_i}\delta N_i - (\ln N_i)\delta N_i \right] = 0$$

Note that the first and third terms on the RHS cancel out and this equation takes a compact form:

$$\sum_{i}\left[\ln N_i - \ln(g_i + N_i)\right]\delta N_i = 0 \qquad (14.9)$$

Recall that Eq. (14.9) is subject to the constraints that N and U are fixed. We can, therefore, rewrite Eqs. (14.7a and b) as

$$\delta N = \sum_{i}\delta N_i = 0 \qquad (14.10a)$$

and
$$\delta U = \sum_{i}\varepsilon_i \delta N_i = 0 \qquad (14.10b)$$

To incorporate the conditions embedded in Eqs. (14.10 a and b) into Eq. (14.9), we use Lagrange's method of undetermined multipliers. As before, we multiply Eqs. (14.10a and b) by α and β, respectively, and add to Eq. (14.9). This leads us to the expression

$$\sum_{i}\left[\ln N_i - \ln(g_i + N_i) + \alpha + \beta\varepsilon_i\right]\delta N_i = 0 \qquad (14.11)$$

As in classical statistics, we use the fact that variations δN_i are arbitrary and cannot be zero. Therefore, for Eq. (14.11) to be satisfied, the coefficient of each term in this equation must vanish identically. Hence, we must have

$$\ln\left(\frac{N_i}{g_i + N_i}\right) = -\alpha - \beta\varepsilon_i \;\Rightarrow\; \frac{1}{1+\dfrac{g_i}{N_i}} = \exp(-\alpha - \beta\varepsilon_i) \;\Rightarrow\; \frac{g_i}{N_i} = \exp(\alpha + \beta\varepsilon_i) - 1$$

or
$$\frac{N_i}{g_i} = \frac{1}{\exp(\alpha + \beta\varepsilon_i) - 1} \qquad (14.12)$$

As before, we put $e^{-\alpha}$ equal to A, the degeneracy parameter. Then Eq. (14.12) can be written as

$$\frac{N_i}{g_i} = \frac{1}{A^{-1}\exp(\beta\varepsilon_i) - 1} \qquad (14.13)$$

Recall that chemical potential (μ) is defined through the relation

$$A = e^{-\alpha} = e^{\beta\mu} \qquad (14.14)$$

In terms of chemical potential, we can rewrite Eq. (14.12) as

$$\frac{N_i}{g_i} = f_{BE}(\varepsilon_i) = \frac{1}{\exp\left[\beta(\varepsilon_i - \mu)\right] - 1} \qquad (14.15)$$

If we treat energy as a continuous variable, the number of particles with energy ε will be given by

$$\frac{N(\varepsilon)}{g(\varepsilon)} \equiv f_{BE}(\varepsilon) = \frac{1}{\exp\left[\beta(\varepsilon - \mu)\right] - 1} \qquad (14.16)$$

This relation is known as **Bose-Einstein distribution function**.

We now summarise the important results of this section.

BOSE-EINSTEIN DISTRIBUTION FUNCTION

- In Bose-Einstein distribution, there is no restriction on the number of particles that can occupy a given state.

- The ways in which N particles can be distributed in M cells is

$$W[N] = \prod_{i=1}^{M} W_i = \prod_i \frac{(g_i + N_i - 1)\,!}{N_i!\,(g_i - 1)\,!}$$

where i^{th} cell contains N_i particles distributed in g_i levels.

- The Bose-Einstein distribution function for the particles with energy ε is given by

$$f_{\text{BE}}(\varepsilon) = \frac{1}{\exp[\,\beta\,(\varepsilon - \mu)\,] - 1}$$

where μ denotes chemical potential.

We now proceed to obtain the Fermi-Dirac distribution function.

14.4 FERMI-DIRAC DISTRIBUTION FUNCTION

To obtain expression for Fermi-Dirac distribution function, we note that fermions obey Pauli's principle and not more than one particle (ignoring spin) can occupy the same energy level. Hence, the number of ways in which we can distribute N_i particles into g_i levels is given by $^{g_i}C_{N_i}$ with $N_i < g_i$. The total number of ways in which we can put N particles into various levels are

$$W[\{N\}] = \prod_i {}^{g_i}C_{N_i} = \prod_i \frac{g_i!}{(g_i - N_i)!\,N_i!} \tag{14.17}$$

As in the case of Bose-Einstein statistics, this distribution is also subject to the conditions that total number of particles in the system and the energy of the system remain constant. That is,

$$\delta N = \sum \delta N_i = 0 \tag{14.18a}$$

and

$$\delta U = \sum \delta N_i \varepsilon_i = 0 \tag{14.18b}$$

As before, we maximise $\ln W$ and set $\delta \ln W = 0$. So on taking logarithm of both sides of Eq. (14.17), we obtain

$$\ln W = \sum_i \left[\, \ln g_i! - \ln(g_i - N_i)\,! - \ln N_i!\, \right] \tag{14.19}$$

Using Stirling's approximation, we write

$$\ln W = \sum_i [\, g_i \ln g_i - g_i - (g_i - N_i)\,\ln(g_i - N_i) + (g_i - N_i)$$

$$- N_i \ln N_i + N_i\,] = \sum_i \left[\, g_i \ln g_i - (g_i - N_i)\ln(g_i - N_i) - N_i \ln N_i\, \right]$$

Note that g_i are constant. Therefore, while differentiating this expression, we get

$$\delta \ln W = \sum_i \left[(N_i - g_i) \frac{1}{(g_i - N_i)}(-\delta N_i) + \delta N_i \ln(g_i - N_i) \right.$$

$$\left. - N_i \frac{1}{N_i} \delta N_i - \ln N_i \delta N_i \right]$$

Note that the first and the third terms on the RHS of this expression cancel out. Then it simplifies to

$$\delta \ln W = \sum_i \left[\ln(g_i - N_i) - \ln(N_i) \right] \delta N_i$$

On equating $\delta \ln W$ to zero, we can write

$$\sum_i \left[\ln(N_i) - \ln(g_i - N_i) \right] \delta N_i = 0 \tag{14.20}$$

This expression is subject to the conditions specified in Eqs. (14.18a and b). To incorporate these and obtain a general expression for most probable distribution, we use Lagrange's method of undetermined multipliers. Therefore, we multiply Eq. (14.18a) by α, Eq. (14.18b) by β and add to Eq. (14.20). This gives

$$\sum_i \left[\ln(N_i) - \ln(g_i - N_i) + \alpha + \beta \varepsilon_i \right] \delta N_i = 0$$

Since δN_i are arbitrary and can be varied independently, we can set the coefficient of each δN_i equal to zero. This gives

$$\ln\left(\frac{N_i}{g_i - N_i} \right) = -\alpha - \beta \varepsilon_i \;\Rightarrow\; \frac{1}{\dfrac{g_i}{N_i} - 1} = \exp(-\alpha - \beta \varepsilon_i) \;\Rightarrow\; \frac{g_i}{N_i} = \exp(\alpha + \beta \varepsilon_i) + 1$$

or

$$\frac{N_i}{g_i} \equiv f_{FD}(\varepsilon_i) = \frac{1}{\exp[\alpha + \beta \varepsilon_i] + 1} = \frac{1}{A^{-1} \exp(\beta \varepsilon_i) + 1} = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] + 1}$$

$$\tag{14.21}$$

where μ defines chemical potential with $A = e^{-\alpha} = e^{\beta \mu}$. Eq. (14.21) is the desired expression for **Fermi-Dirac distribution function**. For continuous distribution, the Fermi-Dirac distribution function $f_{FD}(\varepsilon)$ can be expressed as

$$f_{FD}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1} \tag{14.22}$$

Note that at $T = 0$ ($\beta = \infty$), the exponent in Eq. (14.22) becomes $-\infty$ for $\varepsilon < \mu$, whereas for $\varepsilon > \mu$, the exponent becomes $+\infty$. We can, therefore, rewrite it as

$$f_{FD}(\varepsilon) = \begin{cases} 1 \text{ for } \varepsilon < \mu \\ 0 \text{ for } \varepsilon > \mu \end{cases} \tag{14.23}$$

Mathematically speaking, $f_{FD}(\varepsilon)$ defines a step-function. Physically, it implies that at absolute zero, all levels are occupied up to certain energy, but energy states above it, are empty. This energy is known as *Fermi energy*. We denote it as ε_F. This is shown in curve (i) of Fig. 14.6. Curve (ii) shows the effect of raising the temperature. The curve develops a tail, which is symmetrical about $\varepsilon = \varepsilon_F$. Moreover, at ε_F, $f_{FD}(\varepsilon) = 0.5$.
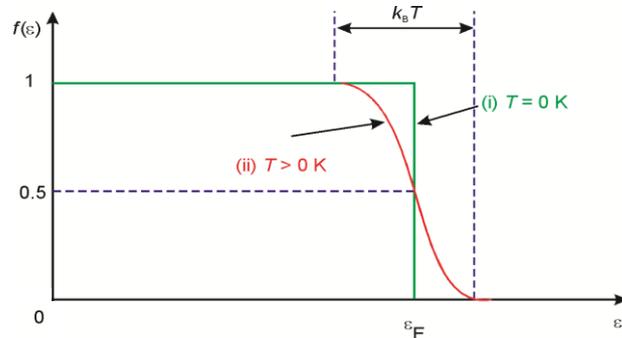

Fig. 14.6: **Plot of Fermi function versus energy at different temperatures.**

At a finite temperature $(T > 0)$, fermions shift to higher energies. However, the width of this region is of the order of $k_B T$. Normally deviations observed from the step-function are important only for those values of ε for which $[\beta(\varepsilon - \mu)]$ is of the order of unity. At higher energies, the exponential term dominates and the F-D distribution function is given by Eq. (14.23).

On the basis of this discussion, we can say that thermal reshuffling of the particles is confined to $k_B T$ around $\varepsilon = \varepsilon_F$. This means that the number of electrons which contribute to thermal properties is proportional to linear power of temperature. Even at room temperature, the product $k_B T$ is quite small; and hence, the major proportion of distribution is not influenced significantly by rise in temperature. Let us sum up important points of this section.

Recap

FERMI-DIRAC DISTRIBUTION FUNCTION

- In F-D statistics, the number of levels g_i is always greater than the number of particles N_i.

- The ways in which N particles can be distributed in M cells is

$$W[N] = \prod_{i=1}^{M} W_i = \prod_i \frac{g_i\,!}{N_i!\,(g_i - N_i)\,!}$$

where i^{th} cell contains N_i particles distributed in g_i levels.

- The Fermi-Dirac distribution function for particles with energy ε is:

$$f_{FD}(\varepsilon) = \frac{1}{\exp[\,\beta\,(\varepsilon - \mu)\,] + 1}$$

where μ denotes chemical potential.

- At absolute zero, F-D distribution is a step-function. At higher temperature, fermions shift to higher energy in the range of $k_B T$ around Fermi energy ε_F with $f_{FD}(\varepsilon_F) = 0.5$.

Before proceeding further, you may like to answer an SAQ.

$\mathcal{SAQ}\,2$ – **Limiting case of B-E and F-D distributions**

Show that in the high energy range, Bose- Einstein as well as Fermi-Dirac distribution reduce to Maxwell-Boltzmann distribution.

Now that we have obtained distribution functions for classical as well as quantum systems, it would be instructive to compare these and get an idea about how particles obeying different statistics behave.

14.5 COMPARISON OF DIFFERENT DISTRIBUTIONS

To compare how different statistics behave, we re-write the expressions for M-B, B-E and F-D distribution functions:

$$f_{MB}(\varepsilon) = \frac{1}{\exp[\beta\,(\varepsilon-\mu)]}$$

$$f_{BE}(\varepsilon) = \frac{1}{\exp[\beta\,(\varepsilon-\mu)]-1}$$

$$f_{FD}(\varepsilon) = \frac{1}{\exp[\beta\,(\varepsilon-\mu)]+1}$$

A closer examination of these expressions reveals that in spite of the vast differences in the assumptions used to arrive at these expressions, they have deceptively similar appearance. In fact, you can combine them into just one expression as

$$f(\varepsilon) = \frac{1}{\exp[\beta\,(\varepsilon-\mu)]+\kappa} \qquad\qquad (14.24)$$

where
$$\kappa = \begin{cases} 0 & M\text{-}B \;\; \text{distribution} \\ +1 & F\text{-}D \;\; \text{distribution} \\ -1 & B\text{-}E \;\; \text{distribution} \end{cases}$$

This logically raises the question: What is the significance of the constant κ in describing the behaviour of a system?

To learn about the enormous consequences of κ, refer to Fig. 14.7, which depicts the distribution functions corresponding to M-B, F-D and B-E statistics.

Note that as compared to M-B distribution, the distribution of bosons is skewed towards lower energy states, whereas fermions are skewed towards higher energy states.

It means that bosons prefer to occupy lower energy states, i.e., live together.
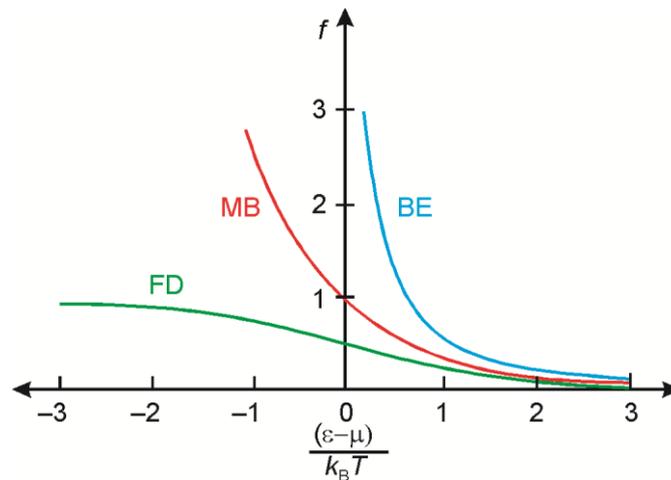
Fig. 14.7: **Plot of B-E, F-D and M-B distribution functions as a function of** $(\varepsilon - \mu) / k_B T$. **Each system is at the same temperature and has the same number of particles.**

In the next two sections, we study some applications of B-E and F-D statistics.

14.6 APPLICATIONS OF BOSE-EINSTEIN STATISTICS

You now know that the spectral distribution of blackbody radiation was first successfully explained by Planck. Though Planck was not convinced of the physical basis of his derivation, Bose derived Planck's law of radiation on the basis of quantum statistics. Einstein extended his ideas to the case of material particles obeying Bose statistics. We begin our discussion with Bose's derivation of Planck's law.

14.6.1 Bose's Derivation of Planck's Law

To begin with, we assume that electromagnetic radiation is enclosed in a cavity of volume V at temperature T. From quantum mechanical point of view, radiation in the cavity can be considered as a collection of photons of different frequencies moving randomly with speed of light. Note that photons of same frequency are indistinguishable and behave as a system of non-interacting particles.

The energy of a photon of frequency ν is taken to be $h\nu$. Moreover, photons have zero rest mass and spin $\hbar$. Further, atoms can emit or absorb photons and the total number of photons is not constant. It means that an assembly of photons is subject to only one constraint, namely $U =$ constant. This essentially means that in Eq. (14.15), we need only one Lagrange multiplier β, i.e., $\alpha = 0$ or $A = 1$. Then Eq. (14.15) can be written as

$$\frac{N_\nu}{g_\nu} = \frac{1}{e^{\beta h\nu} - 1} \qquad (14.25)$$

Let $g_\nu d\nu$ denote the number of quantum states between frequencies ν and $\nu + d\nu$. We can derive the expression for $g_\nu d\nu$ using the principles of quantum mechanics. However, we can obtain the same result using a simple

argument as well. Let us first calculate the number of quantum states in the momentum range p to $p + dp$ and denote it as $g_p dp$. The volume of phase space occupied by a particle in a box of volume V and having momentum between p and $p + dp$ is Vd^3p. In spherical polar coordinates, $d^3p = (p^2 dp \sin\theta d\theta d\phi)$ and integration over θ and ϕ gives 4π. If each cell has volume h^3, we get

$$g_p dp = \frac{4\pi p^2 dp}{h^3} V \qquad (14.26a)$$

From de Broglie's relation between momentum and frequency (or wavelength), we have $p = \dfrac{h}{\lambda} = \dfrac{h\nu}{c}$ and $p^2 dp = \left(\dfrac{h}{c}\right)^3 \nu^2 d\nu.$

On substituting this result in Eq. (14.26a), we can write the number of quantum states in the frequency range ν to $\nu + d\nu$ as

$$g_\nu d\nu = \frac{4\pi V}{c^3} \nu^2 d\nu \qquad (14.26b)$$

Since photons can have two types of polarization, we multiply this by a factor of 2 to obtain

$$g_\nu d\nu = \frac{8\pi V}{c^3} \nu^2 d\nu \qquad (14.27)$$

On using this result in Eq. (14.25), we get the expression for the number of particles in the frequency range ν to $\nu + d\nu$:

$$N_\nu = \frac{8\pi V}{c^3} \frac{\nu^2 d\nu}{e^{\beta h\nu} - 1} \qquad (14.28)$$

If $E_\nu d\nu$ denotes the energy corresponding to the frequency range ν to $\nu + d\nu$, we can write

$$E_\nu d\nu = N_\nu h\nu = \frac{8\pi h V}{c^3} \frac{\nu^3 d\nu}{e^{\beta h\nu} - 1}$$

Note that $E_\nu d\nu$ is a function of volume and therefore depends on the size of the cavity.

So, instead of total energy corresponding to a particular range of frequencies, we prefer energy density. If we represent energy density by $u_\nu d\nu$, we can write

$$u_\nu d\nu = \frac{E_\nu d\nu}{V} = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{\exp(h\nu / k_B T) - 1} \qquad (14.29)$$

Do you recognise this equation? It is identical to Eq. (14.2) and is a mathematical statement of Planck's law. Note that Bose treated electromagnetic radiation as a system of indistinguishable particles and used methods of statistics to understand their behaviour.

Before proceeding further, let us recapitulate the important result obtained in this section.

QUANTUM MECHANICAL DERIVATION OF PLANCK'S LAW

By treating electromagnetic radiation as a system of indistinguishable particles, Bose derived the expression for the energy density as

$$u_\nu d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{\exp(h\nu / k_B T) - 1}$$

14.7 APPLICATIONS OF FERMI-DIRAC STATISTICS

The energy of an F-D system at absolute zero is called **Fermi energy**. As such, it signifies the highest energy level occupied by a fermion at absolute zero. You will now learn how to obtain an expression for Fermi energy.

14.7.1 Fermi Energy

Consider a system of N fermions enclosed in a volume V. According to Pauli's exclusion principle, only one fermion can be accommodated in a given state. You have already learnt that the highest energy possessed by a fermion at absolute zero is known as **Fermi energy**. We will denote it by the symbol ε_F.

To derive an expression for ε_F, we must first know the density of quantum states of a particle with momentum in the interval $\vec{p}$ and $\vec{p} + d\vec{p}$. From Eq. (14.26a,), we recall that this number is $\frac{4\pi V}{h^3} p^2 dp$. Since an electron has two independent spin states, the multiplicity factor (= 2s + 1) will be equal to 2, since $s = 1/2$. So the required density of quantum states is $\frac{8\pi V}{h^3} p^2 dp$.

Hence, the total number of particles is given by

$$N = \frac{8\pi V}{h^3} \int_0^\infty f_{FD} p^2 dp \qquad (14.30)$$

From Eq. (14.23) we recall that

$$f_{FD}(\varepsilon) = \begin{cases} 1 \text{ for } \varepsilon < \mu \\ 0 \text{ for } \varepsilon > \mu \end{cases}$$

We denote the highest momentum at $T = 0$ corresponding to $\varepsilon = \mu$ by p_F.

Then, the upper limit of integration in the integral in Eq. (14.30) changes from ∞ to p_F and we can write

$$N = \frac{8\pi V}{h^3} \int_0^{p_F} p^2 dp \qquad (14.31a)$$

$$= \frac{8\pi V}{h^3} \frac{p_F^3}{3} \tag{14.31b}$$

We invert this relation to obtain the expression for **Fermi momentum**, p_F :

$$p_F = \left(\frac{3N}{8\pi V} \right)^{1/3} h \tag{14.32}$$

This result implies that if we draw a sphere with radius p_F, all the particles will be inside the sphere at absolute zero.

This defines the *Fermi surface*. In the case of alkali and noble atoms, the surface is spherical in shape. In other cases, the shape can be quite complicated.

The energy corresponding to the highest occupied energy level at absolute zero is called **Fermi energy**. It is given by

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \tag{14.33}$$

Now we define *Fermi temperature*, T_F , through the relation

$$T_F = \frac{\varepsilon_F}{k_B} \tag{14.34}$$

In Table 14.1, we have listed values of Fermi energy as well as Fermi temperature for some typical metals.

Note that ε_F varies from 1.58 eV to 14.3 eV; being minimum for cesium and maximum for berylium.

The corresponding Fermi tempratures are of the order 10^4K – 10^5K.

Table 14.1: Values of Fermi energy and Fermi temperature for typical metals

Metal	Fermi energy (eV)	Fermi Temperature $\times 10^4$ **(K)**
Cesium	1.58	1.84
Sodium	3.24	3.77
Calcium	4.69	5.44
Lithium	4.74	5.51
Silver	5.49	6.38
Gold	5.53	6.42
Copper	7.00	8.16
Iron	11.1	13.0
Aluminium	11.7	13.6
Beryllium	14.3	16.6

You should now go through the following example carefully.

$\mathcal{E}$XAMPLE 14.1 : FERMI ENERGY

a) 4.2×10^{21} electrons are confined in a box of volume $1 \, cm^3$. Calculate their Fermi wavelength and Fermi energy.

b) The electrons in the box are replaced by neutrons. How will Fermi wavelength and Fermi energy change? Take $m_e = 9.1 \times 10^{-28}$ g, $m_n = 1.67 \times 10^{-24}$ g and $h = 6.62 \times 10^{-27}$ erg s.

SOLUTION ■ a) From Eq. (14.33), we know that Fermi energy of electrons is given by:

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \Rightarrow p_F^2 = \frac{h^2}{4}\left(\frac{3N}{\pi V}\right)^{2/3}$$

On raising the power of both sides by 3/2, we can write:

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

Now, Fermi wavelength can be expressed as:

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

Note that Fermi wavelength is independent of mass of the fermions.

On substituting the given values, we get

$$\lambda_F = \left(\frac{8 \times 3.1417 \times 1 \, cm^3}{3 \times 4.2 \times 10^{21}}\right)^{1/3} = \left(1.995 \times 10^{-21}\right)^{1/3} cm = 1.26 \times 10^{-7} cm$$

The Fermi energy of electrons can be expressed in terms of Fermi wavelength as

$$\varepsilon_F = \frac{p_F^2}{2\,m} = \frac{1}{2\,m}\left(\frac{h}{\lambda_F}\right)^2 = \frac{1}{(2 \times 9.1 \times 10^{-28}\,g)}\left(\frac{6.62 \times 10^{-27}\,erg\,s}{1.26 \times 10^{-7}\,cm}\right)^2$$

$$= 1.52 \times 10^{-12}\,erg$$

b) Since Fermi wavelength is independent of mass of the particles making up the system, it is not affected when electrons are replaced by neutrons. However, Fermi energy will be equal to

$$\left(\frac{m_e}{m_n}\right)\varepsilon_F = (\varepsilon_F)_{neutron} = \left(\frac{9.1 \times 10^{-28}\,g}{1.67 \times 10^{-24}\,g}\right) \times 1.52 \times 10^{-12}\,erg$$

$$= 8.28 \times 10^{-16}\,erg = 5.18 \times 10^{-4}\,eV$$

To get some practice and test your numerical skills, you should solve an SAQ.

SAQ 3 – **Fermi energy**

Calculate ε_F for copper, if $\dfrac{N}{V} = 8.53 \times 10^{22}$ electrons cm^{-3}. Take the mass of electron $= 9.1 \times 10^{-28}$ g and $h = 6.62 \times 10^{-27}$ erg s.

Zero Point Energy

When a fermion system is in the ground state, all the energy states below the Fermi energy are occupied whereas all the states above Fermi energy are empty. In such a case, the **zero point energy** of a fermion system is obtained by using the relation

$$E_0 = N\varepsilon = N\left(\frac{p^2}{2m}\right)$$

On substituting for N from Eq. (14.31a) and integrating the resultant expression in the range 0 to p_F in the momentum space, we get

$$E_0 = \frac{8\pi V}{h^3} \int_0^{p_F} \frac{p^2}{2m} p^2 dp = \frac{8\pi V}{h^3} \frac{p_F^5}{10m}$$

$$= \frac{8\pi V}{5h^3} p_F^3 \varepsilon_F$$

On combining this result with Eq. (14.31b), we obtain the expression for zero point energy of a fermion system:

$$E_0 = \frac{3}{5} N\varepsilon_F \qquad\qquad\qquad (14.35)$$

The mean energy per fermion at absolute zero is given by

$$\bar{\varepsilon} = \frac{E_0}{N} = \frac{3}{5}\varepsilon_F \qquad\qquad\qquad (14.36)$$

For conduction electrons in copper

$$\bar{\varepsilon} = \frac{3}{5} \times (7.0\,\text{eV}) = 4.2\,\text{eV}$$

This energy corresponds to several thousand kelvin to which an electron, if treated classically, would have to be raised. This shows that unlike a classical particle, a fermion has appreciable energy even at absolute zero!

This justifies our statement that a fermion system is quite alive even at absolute zero.

This is a quantum effect arising out of the Pauli's exclusion principle and brings out the inadequacy of classical statistics in describing the behaviour of electrons at temperatures far below their Fermi temperature ($T \ll T_F$).

Now you may ask: Is it true for pressure also? To learn the answer to this question, you should solve the following SAQ.

$SAQ\,4$ – **Pressure exerted by a fermion system**

The pressure exerted by a fermion system at absolute zero is equal to $\frac{2}{5}\left(\frac{N}{V}\right)\varepsilon_F$. Using the data obtained in SAQ 3, calculate the pressure exerted by the electrons in a copper wire.

On working out SAQ 4, you will realise that the pressure exerted by electrons in a copper wire comes out to be huge; of the order of 10^5 atm. Do we feel such an enormous pressure when we hold a copper wire in our hand? If not, why? It is because this pressure is counter-balanced by Coulomb attraction of electrons by ions.

Before proceeding further, let us recapitulate what we have learnt in this section.

Recap

FERMI ENERGY

- The maximum energy possessed by fermions at absolute zero is known as Fermi energy. It is given by

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

- Typical values of Fermi energy of metals range from 2 to 15 eV. The corresponding Fermi temperatures are about 10^4 to 10^5 K.

- Electron gas in a metal exerts extremely high pressure ($\sim 10^5$ atm), which is balanced by the Coulomb forces within the material.

We have so far considered an F-D system at absolute zero. Such a system is said to be completely degenerate. You may like to know how thermodynamic properties such as heat capacity and entropy of a F-D system vary with temperature. For simplicity, we confine our discussion to the behaviour of electrons. You will recall that for $T \ll T_F$, f_{FD} does not differ much from the value at $T = 0$ K. Now, for conduction electrons in metals, T_F is of the order of 10^4 to 10^5 K. This means that conduction electrons are in extremely degenerate state even under normal conditions and very few of them are free to move. As such, most of the electrons in a metal are tightly bound in low lying states and do not contribute to conduction.

We will refrain from discussing the behaviour of electrons in metals in detail. However, very simple arguments can be used to understand the heat capacity of metals. You will learn it now.

14.7.2 Electronic Heat Capacity

In Sec 14.2, you have learnt that in the classical regime, the correct explanation of temperature variation of heat capacity of metals, particularly at low values, puzzled physicists for quite some time. The underlying reason is

that electrons are fermions and obey F-D statistics. The electronic heat capacity varies linearly at low temperatures. In fact, heat capacity of a metal is a sum of two parts: (i) an electronic contribution, which is proportional to T and dominates at low temperatures and (ii) the lattice contribution, which is proportional to T^3 and dominates at room temperature and above:

$$C_V = aT + bT^3 \qquad\qquad (14.37)$$

Experiments show that the contribution of electronic heat capacity is about 1% of the total.

Let us now summarise what you have learnt in this unit.

14.8 SUMMARY

Concept	Description
Bose-Einstein distribution function	■ The **Bose-Einstein distribution** function is given by $$\frac{N_i}{g_i} = \frac{1}{\exp\left[\beta\left(\varepsilon_i - \mu\right)\right] - 1}$$ For continuous distribution, we can write $$f_{BE} = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{\exp\left[\beta\left(\varepsilon - \mu\right)\right] - 1}$$
Fermi-Dirac distribution function	■ The **Fermi-Dirac distribution** function is given by $$\frac{N_i}{g_i} = \frac{1}{\exp\left[\beta\left(\varepsilon_i - \mu\right)\right] + 1}$$ For continuous distribution, we can write $$f_{FD}(\varepsilon) = \frac{1}{\exp\left[\beta\left(\varepsilon - \mu\right)\right] + 1}$$
Spectral energy density as per Planck's law for blackbody radiation	■ According to **Planck's law** of blackbody radiation, the spectral energy density is given by $$u_\nu d\nu = \left(\frac{8\pi h}{c^3}\right)\frac{\nu^3}{\exp\left(\dfrac{h\nu}{k_B T}\right) - 1}\, d\nu$$
Fermi energy	■ The **Fermi energy** of a fermion is given by: $$\varepsilon_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}$$
Pressure exerted by F-D gas at $T = 0$ K	■ The pressure exerted by F-D gas at $T = 0$ K is: $$p_F = \frac{2}{5}\left(\frac{N}{V}\right)\varepsilon_F$$

Electronic heat capacity

■ The electronic contribution to the heat capacity of a metal is given by

$$C_V = aT + bT^3$$

14.9 TERMINAL QUESTIONS

1. Explain on the basis of statistical mechanics the reason for different properties observed in case of liquid ^{3}He and liquid ^{4}He.

2. Estimate the deviation in the value of heat capacity C_V from the value predicted by the Dulong-Petit's law for a metallic sample kept at its Einstein temperature.

3. Three particles are to be distributed in 4 states. Calculate the number of ways this distribution can be done if the particles obey (i) M-B, (ii) B-E and (iii) F-D statistics.

4. Calculate the Fermi energy and Fermi temperature for:

   i) liquid ^{3}He assuming that each atom occupies 63 Å^3 volume and mass of ^{3}He is equivalent to mass of 3 protons; and

   ii) electrons in a white dwarf star consisting of completely ionized He atoms with density $\rho = 10^7 \, \text{g cm}^{-3}$ and number density 10^{30} electrons per cm^3.

5. The number density of gold atoms is 5.9×10^{28} atoms m^{-3}. Each atom contributes one free electron for conduction. Examine, whether the electron gas is strongly degenerate at room temperature.

14.10 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. A particle consisting of an odd number of Fermi particles is a fermion and a particle consisting of an even number of Fermi particles is a boson. ^{3}He consists of two protons, one neutron, and two electrons. Hence, it consists of five particles of spin ½, and is a fermion. ^{4}He consists of two protons, two neutrons and two electrons. Hence, it consists of six fermions and is a boson.

2. In the high energy region, we can write $\varepsilon >> \mu,$ so that $\beta(\varepsilon - \mu) >> 1$ and then we can ignore unity in comparison to the exponential function in [Eqs. (14.16) and (14.22)]. Then Bose-Einstein as well as Femi-Dirac distribution functions reduce to Maxwell-Boltzmann distribution function.

3. We have

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

On substituting the given values in the expression of ε_F, we get

$$\varepsilon_F = \frac{(6.62 \times 10^{-27}\,\text{erg s})^2}{2 \times 9.1 \times 10^{-28}\,\text{g}} \left(\frac{3}{8\pi} \times 8.53 \times 10^{22}\,\text{cm}^{-3} \right)^{2/3} = 11.31 \times 10^{-12}\,\text{erg}$$

By using the relation $1\,\text{erg} = 6.24 \times 10^{11}\text{eV}$, we can express the Fermi energy in the units of electron volts as 7.1 eV.

4. From SAQ 3, we know that for copper, $\frac{N}{V} = 8.53 \times 10^{28}$ electrons m^{-3} and

$\varepsilon_F = 11.31 \times 10^{-19}$ J. Substituting these values in the given expression, we

get pressure $= \frac{2}{5} \left(\frac{N}{V} \right) \varepsilon_F = 3.86 \times 10^{10}\,\text{N m}^{-2} = 3.86 \times 10^5\,\text{atm}$.

Terminal Questions

1. ^{3}He and ^{4}He, the two stable isotopes of helium, have markedly different behaviour at low temperatures. The ^{4}He atom (comprising of two protons, two neutrons and two electrons) has integral spin and is governed by Bose-Einstein statistics. At about 2.18 K and $p \sim 1$ atm, it undergoes λ-transition, which was explained by F. London as Bose-Einstein condensation. Above the λ-transition temperature, it behaves like a regular, "normal" fluid However, below the λ-transition temperature, helium behaves as a super-fluid characterized by zero viscosity.

2. For $T = \theta_E$, Eq. (14.3b) implies that

$$C_V = 3R \left(\frac{\theta_E}{\theta_E} \right)^2 \frac{\exp(\theta_E / \theta_E)}{\left[\exp(\theta_E / \theta_E) - 1 \right]^2}$$

$$= 3R \frac{e}{(e-1)^2} = 3R \frac{2.718}{(2.718-1)^2} = 3R(0.92)$$

Hence, the deviation from the value predicted by Dulong-Petit's law
is $\Delta C_V = 3R(1 - 0.92) = 0.24R$

3. i) For M-B statistics, the particles are distinguishable. Hence, the number of ways are $4^3 = 64$.

    ii) For B-E statistics, the particles are indistinguishable and any number of them can occupy the same state.

    Hence, the number of ways they can be distributed are:
    $$^{3+4-1}C_3 = \frac{6!}{3!\,3!} = 20$$

    iii) For F-D statistics, the particles are indistinguishable and maximum only one particle can occupy any state. The number of ways are:
    $$^4C_3 = \frac{4!}{3!\,1!} = 4$$

4. We have

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

and $T_F = \dfrac{\varepsilon_F}{k_B} = \dfrac{h^2}{2m\,k_B}\left(\dfrac{3N}{8\pi V}\right)^{2/3}$

i) For liquid ^{3}He, $\dfrac{V}{N} = 63\,\text{Å}^3\ \text{atom}^{-1} = 63\times10^{-24}\ \text{cm}^3\ \text{atom}^{-1}$

$\therefore\quad \dfrac{N}{V} = \dfrac{10^{24}}{63} = 1{.}59\times10^{22}\ \text{atom}\,\text{cm}^{-3}$

$m = 3\times \text{mass of proton} = 3\times1.67\times10^{-24}\text{g} = 5.01\times10^{-24}\text{g}$

$\therefore\ \varepsilon_F = \dfrac{(6.62\times10^{-27}\,\text{erg s})^2}{2\times5.01\times10^{-24}\text{g}}\left(\dfrac{3}{8\pi}\times15.9\times10^{21}\ \text{cm}^{-3}\right)^{2/3}$

$= 6.71\times10^{-16}\,\text{erg}$

$= 6.71\times10^{-16}\times6.24\times10^{11}\ \text{eV} = 0.42\,\text{meV}$

This yields, $T_F = \dfrac{\varepsilon_F}{k_B} = \dfrac{6.71\times10^{-16}\,\text{erg}}{1.38\times10^{-16}\,\text{erg}\,\text{K}^{-1}} = 4.9\,\text{K}$

ii) For white dwarfs $\rho = 10^7\text{g cm}^{-3}$ and $\dfrac{N}{V} = 10^{30}\ \text{cm}^{-3}$

$\therefore\ \varepsilon_F = \dfrac{(6.63\times10^{-27}\,\text{erg s})^2}{2\times9.1\times10^{-28}\text{g}}\left(\dfrac{3}{8\pi}\times10^{30}\ \text{cm}^{-3}\right)^{2/3}$

$= 5.84\times10^{-7}\,\text{erg} = \dfrac{5.84\times10^{-7}\,\text{erg}}{1.6\times10^{-12}\ \text{erg}\,\text{eV}^{-1}} = 0.36\,\text{MeV}$

and Fermi temperature $= = \dfrac{5.85\times10^{-7}\,\text{erg}}{1.38\times10^{-16}\ \text{erg K}^{-1}} = 4.23\times10^{9}\text{K}$

5. To obtain the Fermi temperature, we first calculate the Fermi energy of gold.

$$\varepsilon_F = \dfrac{h^2}{2m}\left(\dfrac{3N}{8\pi V}\right)^{2/3}$$

Substituting the values of the various terms,

$$\varepsilon_F = \dfrac{(6.62\times10^{-34}\,\text{J s})^2}{2\times9.1\times10^{-31}\ \text{kg}}\left(\dfrac{3}{8\pi}\times5.9\times10^{26}\ \text{m}^{-3}\right)^{2/3}$$

$$= 8.85\times10^{-19}\ \text{J}\,(= 5.53\,\text{eV})$$

Now, the Fermi temperature is related to Fermi energy with the relation

$$T_F = \dfrac{\varepsilon_F}{k_B}$$

$$= \dfrac{8.85\times10^{-19}\ \text{J}}{1.38\times10^{-23}\ \text{J K}^{-1}} = 6.41\times10^{4}\ \text{K}$$

Since the Fermi temperature for gold is far greater than the room temperature, the electron gas in the gold sample is strongly degenerate.

FURTHER READINGS

1. **Thermal Physics: Kinetic Theory, Thermodynamics and Statistical Mechanics** by Garg, S.C., Bansal, R.M. and Ghosh, C.K., McGraw Hill Education (India) Pvt. Ltd., 2nd Edition, Seventh Reprint (2018).

2. **A Treatise on Heat** by Saha, M.N. and Srivastava, B.N., The Indian Press, 5th Edition (1969).

TABLE OF PHYSICAL CONSTANTS

Symbol	Quantity	Value
c	Speed of light in vacuum	3.00×10^8 ms^{-1}
μ_0	Permeability of free space	1.26×10^{-6} NA^{-2}
ε_0	Permittivity of free space	8.85×10^{-12} C^{2}N^{-1}m^{-2}
$1/4\pi\varepsilon_0$		8.99×10^9 Nm^{2}C^{-2}
e	Charge of the proton	1.60×10^{-19} C
$-e$	Charge of the electron	-1.60×10^{-19} C
h	Planck's constant	6.63×10^{-34} Js
$\hbar$	$h/2\pi$	1.05×10^{-34} Js
m_e	Electron rest mass	9.11×10^{-31} kg
$-e/m_e$	Electron charge to mass ratio	-1.76×10^{11} Ckg^{-1}
m_p	Proton rest mass	1.67×10^{-27} kg (1 amu)
m_n	Neutron rest mass	1.68×10^{-27} kg
a_0	Bohr radius	5.29×10^{-11} m
N_A	Avogadro constant	6.02×10^{23} mol^{-1}
R	Universal gas constant	8.31 Jmol^{-1}K^{-1}
k_B	Boltzmann constant	1.38×10^{-23} JK^{-1}
G	Universal gravitational constant	6.67×10^{-11} Nm^{2}kg^{-2}

LIST OF BLOCKS AND UNITS: BPHCT-135

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SYLLABUS: THERMAL PHYSICS AND STATISTICAL MECHANICS (BPHCT-135)

4 Credits

Kinetic Theory of Gases: Expression for pressure (no derivation), kinetic interpretation of temperature and derivation of gas laws, real gases (van der Waals equation, qualitative discussion). Derivation of Maxwell's law of distribution of velocities and its experimental verification, expression for average speed $(\bar{v})$, most probable speed (v_p), and root mean square (v_{rms}), law of equipartition of energy (no derivation) and its applications to specific heat of gases, monoatomic and diatomic gases. Mean free path (zeroth order). Transport phenomena, viscosity, conduction and diffusion (discussion of physical implications only, no derivation). Brownian motion (no derivation) and its significance, sedimentation, Perrin's experiment.

The Zeroth Law and The First Law of Thermodynamics: Boundaries, variables, processes (reversible and irreversible), graphical description. Statement of zeroth law, introduction of concept of temperature, applications of the zeroth law. Compressibility and expansion coefficient. First law of thermodynamics, statement, parametric form, mathematical form (integral and differential), relation between c_p and c_v, work done during isothermal and adiabatic processes, velocity of sound.

The Second and Third Law of Thermodynamics: Heat engines, conversion of heat into work, Carnot cycle, efficiency of a Carnot engine, Carnot theorem, Kelvin-Planck and Clausius statements of second law of thermodynamics, equivalence of Kelvin-Planck and Clausius statements. Entropy, second law and entropy, entropy changes in reversible and irreversible processes, entropy-temperature diagram, statement and consequences of the third law of thermodynamics (unattainability of absolute zero temperature, etc.). Thermodynamic potentials, enthalpy, Gibbs, Helmholtz and internal energy functions, Maxwell's relations and their applications, Clausius-Clapeyron equation, Joule Thomson effect, *TdS* equations. Black body radiation, spectral distribution, concept of energy density, derivation of Planck's law, deduction of laws of radiation (Wien's distribution law, Rayleigh-Jeans law, Stefan Boltzmann law and Wien's displacement law).

Statistical Mechanics: Phase space, macrostate and microstate, entropy and thermodynamics probability, distribution function. Maxwell-Boltzmann law, partition function of a monoatomic gas and deduction of thermodynamic functions. Need for quantum statistics, Bose-Einstein distribution function, Bose-Einstein photon gas, Fermi-Dirac distribution function, strongly degenerate Fermi system, Fermi energy, electronic heat capacity, comparison of the three statistics.