

# **Fundamentals of STATISTICAL MECHANICS**

**(SECOND EDITION)**

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Published by New Age International (P) Ltd., Publishers

First Edition: 1998

Second Edition: 2012

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E-mail: chennai@newagepublishers.com
  - CC-39/1016, Carrier Station Road, Ernakulam South, Cochin-682 016. Tel.: (0484) 2377004, Telefax: 4051303  
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Telefax: 2543669, E-mail: guwahati@newagepublishers.com
  - 105, 1st Floor, Madhiray Kaveri Tower, 3-2-19, Azam Jahi Road, Nimboliadda, Hyderabad-500 027  
Tel.: (040) 24652456, Telefax: 24652457, E-mail: hyderabad@newagepublishers.com
  - RDB Chambers (Formerly Lotus Cinema) 106A, 1st Floor, S.N. Banerjee Road, Kolkata-700 014  
Tel.: (033) 22273773, Telefax: 22275247, E-mail: kolkata@newagepublishers.com
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E-mail: lucknow@newagepublishers.com
  - 142C, Victor House, Ground Floor, N.M. Joshi Marg, Lower Parel, Mumbai-400 013. Tel.: (022) 24927869  
Telefax: 24915415, E-mail: mumbai@newagepublishers.com
  - 22, Golden House, Daryaganj, New Delhi-110 002. Tel.: (011) 23262370, 23262368, Telefax: 43551305  
E-mail: sales@newagepublishers.com
- 

**ISBN: 978-81-224-3278-7**

**₹ 295.00**

**C-11-09-5849**

Printed in India at Paramanand Offset, Delhi.

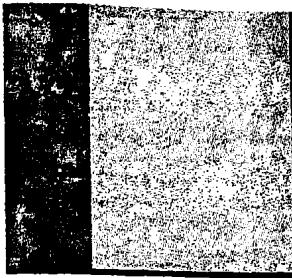
Typeset by In-house.

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## **PREFACE TO THE SECOND EDITION**

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The popularity of the book, *Fundamentals of Statistical Mechanics* has gained over the years and as per our commitment to bring in excellence in our books, this edition, has been thoroughly checked and suggestions by the esteemed readers incorporated. With the amplification and removal of printer's errors of rubric, as necessary, this will present easy to read material for students of physics and engineering. We will greatly appreciate helpful specific suggestions from teachers of the subject so as to enhance the usefulness of the book for the students.

**—Publisher**

## PREFACE TO THE FIRST EDITION

Statistical mechanics is an indispensable formalism in the study of physical properties of matter in bulk. It has led to a better understanding of foundations of thermodynamics and is a very elegant mathematical framework capable of presenting a clear picture of many a physical phenomena. Basic knowledge of this subject is, therefore, essential for every student of physics, whatever may be the field of his specialization.

Though several excellent accounts have been written on the subject, many of them are either too brief or too highly mathematical. Hence, there appears to be a need for an up-to-date, compact and inexpensive book on statistical mechanics, treating the subject in an introductory manner, specially adapted for the beginner in the field and also to those who require a modest working knowledge of this subject because of its application to other fields. The desire to meet this situation gave me an incentive in 1981 to write the book *Introduction to Statistical Mechanics*.

During the decade that has passed since its appearance, the book was widely used and well-received by students and teachers who made very useful comments and offered suggestions for its improvement. Keeping these in mind, I decided to rewrite the book and amplify it considerably. Although the framework of the earlier book has been retained, in this new book most of the sections have been re-written and expanded. In Chap 11, theories of phase transitions have been discussed along with their range of validity. Other topics such as chemical equilibrium and Saha ionization formula have also been included in this chapter. The method used by Maxwell before the advent of Gibbs statistics, to derive his velocity distribution has been described in Chap 3 to satisfy student's curiosity. A chapter on Basic concepts of Probability has been included which is of auxiliary nature and may be omitted by those who are acquainted with the theory of probability.

I have been very selective in the choice of topics to be included. The emphasis is on the fundamentals together with some instructive and useful applications. In a book of this size it has not been possible to deal exhaustively with all applications. Some typical cases have been selected

with all applications. Some typical cases have been selected and described so that all the important methods of dealing with any particular problem can be studied. An Attempt has been made to emphasize the physical basis of the subject, but without undue neglect of its mathematical aspects. The book, thus, bridges the gap between highly mathematical works and the usual less rigorous formulations of the subject. Problems are given at the end of each chapter. These are meant to be read as integral part of the text. They present a number of applications and also serve to illuminate techniques.

In preparing this book, I have consulted a large number of books by various authors to whom I am grateful. A list of some of these is given at the end.

I should like to thank Dr. P.V. Panat, Professor of Physics, University of Poona, who offered some useful suggestions, and my students on whom the material of the book has been tried out. I wish to express my sincere appreciation to my wife for her forbearance whilst this book was being written.

—Author

# CONTENTS

*Preface to the Second Edition*

(v)

*Preface to the First Edition*

(vii)

## Chapter 1: Introduction

1-4

## Chapter 2: Basic Concepts of the Theory of Probability 5-34

2.1 Random Events	5
2.2 Probability	6
2.3 Probability and Frequency	7
2.4 Probability from an Ensemble	7
2.5 Some Basic Rules of Probability Theory	8
2.5.1 Summation Rule	8
2.5.2 Corollary	11
2.5.3 Multiplication Rule: Joint Probability	11
2.5.4 Conditional Probability	12
2.6 Continuous Random Variables	14
2.7 Probability for a Molecule to Lie in a Finite Volume	16
2.8 Mean Value of a Discrete Random Variable	16
2.9 Mean Value of a Continuous Random Variable	17
2.10 Variance : Dispersion	18
2.11 Probability Distribution	19
2.12 Binomial Distribution	20
2.13 Mean Value When the Distribution is Binomial	23
2.14 Fluctuations	23
2.15 Stirling Approximation	24
2.16 Poisson Distribution	26
2.17 Mean Values and Standard Deviation in the Case of Poisson Distribution	27

---

2.18 Gaussian Distribution	27
2.19 Standard Deviation in the Case of Gaussian Distribution	31
2.20 Random Walk Problem	31
<i>Problems</i>	34

## **Chapter 3: Maxwell Distribution** **35–48**

3.1 Maxwell Velocity Distribution	35
3.2 Momentum Distribution	38
3.3 Energy Distribution	38
3.4 Some Significant Mean Values	39
3.5 Experimental Verification of Maxwell Distribution	41
3.5.1 Stern's Experiment	41
3.5.2 Free Fall under Gravity	42
3.5.3 The Doppler Broadening of Spectral Lines	43
3.6 Fraction of Molecules in a Gas with Energies Higher than a Certain Value $\varepsilon_0$	44
<i>Problems</i>	48

## **Chapter 4: Macroscopic and Microscopic States** **49–65**

4.1 Macroscopic States	49
4.2 Microscopic States	50
4.3 Phase Space	51
4.4 The $\mu$ -space	55
4.5 The $G$ -space	56
4.6 Postulate of Equal a Priori Probabilities	57
4.7 Ergodic Hypothesis	57
4.7.1 Mean Value Over an Ensemble	58
4.7.2 Mean Value Over Time	58
4.8 Density Distribution in Phase Space	59
4.9 Liouville's Theorem	61
4.10 Principle of Conservation of Density in Phase and Principle of Conservation of Extension in Phase	63
4.11 Condition for Statistical Equilibrium	64
<i>Problems</i>	65

## **Chapter 5: Statistical Ensembles** **66–86**

5.1 Microcanonical Ensemble	66
5.2 Canonical Ensemble	67

---

5.3 Alternative Method for the Derivation of Canonical Distribution	70
5.4 Mean Value and Fluctuations	74
5.5 Grand Canonical Ensemble	75
5.6 Alternative Derivation of the Grand Canonical Distribution	76
5.7 Fluctuations in the Number of Particles of a System in a Grand Canonical Ensemble	77
5.8 Reduction of Gibbs Distribution to Maxwell and Boltzmann Distributions	78
5.8.1 Maxwell Distribution	78
5.8.2 Boltzmann Distribution	81
5.9 Barometric Formula	82
5.10 Experimental Verification of the Boltzmann Distribution	83
5.11 Mixture of Gases	83
<i>Problems</i>	85

## Chapter 6: Some Applications of Statistical Mechanics

87-124

6.1 Rotating Bodies	87
6.2 The Probability Distribution for Angular Momenta and Angular Velocities of Rotation of Molecules	89
6.3 Thermodynamics	90
6.3.1 Reversible and Irreversible Process	90
6.3.2 The Laws of Thermodynamics	91
6.4 Statistical Interpretation of the Basic Thermodynamic Variables	93
6.4.1 Energy and Work	93
6.4.2 Pressure	94
6.4.3 Entropy	94
6.4.4 Change in Entropy with the Change in Volume	96
6.4.5 Change in Entropy with the Change in Temperature	96
6.4.6 Entropy for Adiabatic Processes	97
6.4.7 Entropy in Terms of Probability	98
6.4.8 Additive Property of Entropy	99
6.4.9 Helmholtz Free Energy	99
6.5 Physical Interpretation of $\alpha$	100
6.6 Chemical Potential in the Equilibrium State	101
6.7 Thermodynamic Functions in Terms of the Grand Partition Function	102
6.8 Ideal Gas	103

6.9 Gibbs Paradox	106
6.10 The Equipartition Theorem	109
6.11 The Statistics of Paramagnetism	111
6.11.1 Potential Energy of a Magnetic Dipole in a Magnetic Field	111
6.11.2 Curie's Law	112
6.12 Thermal Disorder in a Crystal Lattice	116
6.13 Non-ideal Gases	117
<i>Problems</i>	123

## **Chapter 7: Formulation of Quantum Statistics 125–133**

7.1 Density Matrix	125
7.2 Liouville's Theorem in Quantum Statistical Mechanics	128
7.3 Condition for Statistical Equilibrium	129
7.4 Ensembles in Quantum Mechanics	130
<i>Problems</i>	133

## **Chapter 8: Bose-Einstein and Fermi-Dirac Distribution**

**134–155**

8.1 Symmetry of Wave Functions	134
8.2 The Quantum Distribution Functions	139
8.3 The Boltzmann Limit of Boson and Fermion Gases	143
8.4 Evaluation of the Partition Function	144
8.5 Partition Function for Diatomic Molecules	146
(a) Translational Partition Function	146
(b) Rotational Partition Function	146
(c) Vibrational Partition Function	149
(d) Electronic Partition Function	150
8.6 Equation of State for an Ideal Gas	151
8.7 The Quantum Mechanical Paramagnetic Susceptibility	152
<i>Problems</i>	154

## **Chapter 9: Ideal Bose Systems**

**156–176**

9.1 Photon Gas	156
9.2 Einstein's Derivation of Planck's Law	161
9.3 Bose-Einstein Condensation	163
9.4 Specific Heat from Lattice Vibration	168
9.5 Debye's Model of Solids : Phonon Gas	170
<i>Problems</i>	175

**Chapter 10: Ideal Fermi Systems****177-201**

10.1 Fermi Energy	177
10.2 An Alternate Derivation of Fermi Energy	179
10.3 Mean Energy of Fermions at $T = 0$ K	180
10.4 Fermi Gas in Metals	181
10.5 Atomic Nucleus as an Ideal Fermion Gas	182
10.6 Fermi Energy as a Function of Temperature	183
10.7 Electronic Specific Heat	188
10.8 White Dwarfs	190
10.9 Compressibility of Fermi Gas	197
10.10 Pauli Paramagnetism	198
10.11 A Relativistic Degenerate Electron Gas	199
<i>Problems</i>	200

**Chapter 11: Phase Equilibria****202-225**

11.1 Equilibrium Conditions	202
11.2 Classification of Phase Transitions	204
11.3 Phase Diagram	205
11.4 Clausius-clapeyron Equation	207
11.5 Van der Waal's Equation	210
11.6 Second-order Phase Transitions	213
11.7 Ginzburg-landau (gl) Theory	214
11.8 Phase Transition in Ferromagnetic Materials	217
11.9 Liquid Helium	219
11.10 Chemical Equilibrium	221
11.11 Condition for Chemical Equilibrium	221
11.12 The Law of Mass Action	222
11.13 Saha Ionization Formula	223
11.14 Dissociation of Molecules	224
<i>Problems</i>	225

**Chapter 12: Transport Phenomena****226-251**

12.1 Mean Collision Time	226
12.2 Scattering Cross-section	227
12.3 Viscosity	231
12.4 Electrical Conductivity	234
12.5 Thermal Conductivity	235
12.6 Thermionic Emission	237

---

12.7 Photoelectric Effect	239
12.8 Molecular Collisions	240
12.9 Effusion	243
12.10 Diffusion	244
12.11 Brownian Motion	246
12.12 Einstein's Relation for Mobility	248
<i>Problems</i>	250

**Chapter 13: General Theory of Transport Phenomena****252-267**

13.1 Distribution Function	252
13.2 Boltzmann Transport Equation	253
13.3 Relaxation Approximation	254
13.4 Electrical Conductivity from the Relaxation Approximation	255
13.5 A Rigorous Formulation of the Transport Theory	257
13.6 Boltzmann's Theorem	259
13.7 Maxwell-Boltzmann Distribution from Boltzmann's Equation	261
13.8 H Theorem in Quantum Mechanics	262
13.9 Variation of Mean Values	264
13.10 The Laws of Conservation	266
<i>Problems</i>	267

**Appendix****268-273****Appendix A**

The method of Lagrangian undetermined multipliers

268

**Appendix B**

Some useful integrals

269

**Appendix C**

1. physical constants

271

2. Conversion factors

271

**Answers to Problems**

271

**Bibliography****274-275**

## INTRODUCTION

We encounter in nature, physical systems comprising a large number of microentities such as atoms, molecules, electrons, photons, etc. These are *macroscopic systems*—systems large compared to atomic dimensions. A macroscopic system may be a solid, a liquid, a gas, an electromagnetic radiation consisting of a ‘gas of photons’, a ‘gas of electrons’ inside a metallic conductor or any other. We are interested in the bulk properties of these systems. Statistical mechanics consists the study of the properties and behaviour of these systems.

But is there, really, any need for a ‘new mechanics’ for this purpose? Can we not obtain the information we are seeking, with the help of disciplines we are already familiar with? Will not the laws of quantum mechanics, which describe all known natural phenomena, be able to provide the desired information? The properties of a macroscopic system depend upon the properties of the particles that make up the system and on the way in which they interact with each other. The dynamical behaviour of the particles can be described using the laws of quantum mechanics. Interactions between atoms, molecules, etc., are also now fairly well understood. It would be reasonable, therefore, to expect to derive all knowledge of a macroscopic system through the study of the behaviour of their constituent particles.

This reasoning seems to be quite sound and it is, indeed, true in principle, that we can obtain complete information concerning the motion of a mechanical system by constructing and integrating the equations of motion of its constituent particles. But such a dynamical description of the many-particle system is technically unrealizable.

Consider, for example, a mole of a gas. Gas is the simplest of the three forms of matter and mole is a relatively small volume of matter. The number of molecules in a mole of any gas is the Avogadro number  $N_A = 6.02 \times 10^{23}$ . Suppose we set on constructing and integrating the equations of motion of the molecules in mole. For describing the motion of each molecule we must know its initial position and velocity. The position is determined by the coordinates  $x, y, z$  and the velocity by the three components  $v_x, v_y, v_z$ . We, therefore, have to fix  $6 \times 6.02 \times 10^{23}$  numbers, i.e., more than 3,000,000,000,000,000,000,000 numbers in

order to describe the position and velocities of all the molecules at a *particular instant*. Suppose we have with us an instrument which can register numbers at the rate of  $10^9$  per second. Even at this rate, it would take  $6 \times 6.02 \times 10^{17}$  s, i.e., about  $10^{11}$  years. This is a hopeless undertaking!

But it is not just this circumstance that makes such a dynamic consideration impractical. The main trouble is that the solution of the equation of motion requires a statement of the initial values of all the variables and we cannot record sufficient data on the initial position and momenta of all atoms at a particular instant. Even the problem of an atom with two electrons presents such great mathematical difficulties that no one so far has been able to solve it completely. Hence, should one even be able to construct and integrate the equation of motion, it will not be possible for him to obtain an exact solution for want of precise knowledge about initial velocities and position coordinates of the particles constituting the system.

Besides, complexities arising from a large number of constituent particles can often give rise to some unexpected behaviour of the system, which cannot be described either by the methods of classical or those of quantum mechanics. To illustrate this observation, the following examples can be given.

- (i) A gas of identical single atoms such as helium, abruptly condenses under certain conditions to form a liquid with very different properties. This is difficult to understand on the basis of the properties of individual molecules.
- (ii) We know that heat flows from warmer to cooler bodies. The reverse flow is not attained except by input of energy. Can an exact knowledge of the positions and velocities of molecules explain the irreversibility of heat flow? One does not have to know the coordinates and velocities of the particles of a metal rod in order to explain why heat spreads from the hot end to the cold. The kinetic theory explains heat to be a result of random motion and collisions of molecules. The laws of mechanics, no doubt, govern collision between molecules and may give us a complete microscopic picture; but they do not agree with the concept of irreversibility.

In order to tide over this difficulty, can we not investigate a many-particle system without going into its internal structure? We have adopted this technique in thermodynamics, which is distinguished by its simplicity and leads to very accurate results. But thermodynamic method is essentially a phenomenological method. Its object is to establish a relationship between directly observed quantities, such as pressure, volume and temperature. It does not deal with the internal mechanism of the processes determining the behaviour of the system. Thermodynamic laws which govern the behaviour of large molecular population, are not concerned with the fate of individual molecules. The internal mechanisms

remain unknown. For example, it cannot explain why a copper wire cools upon rapid expansion while a rubber, under similar conditions, becomes hot.

It is, therefore, expedient to formulate some special laws, starting from some basic notions of atomic theory, which would lead to a coherent conceptual framework capable of describing and predicting the properties of microscopic systems. How could this be possible? One would expect the complexity of the properties of a mechanical system to increase with the increase in the number of its constituent particles. Fortunately, however, these complexities lead to some definite regularities, in the properties of the system, which can be treated adequately and appropriately by formulating some special laws — *statistical laws*. With the help of these laws it has become possible to describe the macroscopic properties of a system in terms of microscopic properties of its constituent particles without involving the detailed calculation of motion of individual particles. Although one has started from an incomplete knowledge of the initial state of a system; statistical mechanics, or the basis of laws formulated, enables him to make predictions regarding the future condition of the system — which hold on an average and are true to a very high degree of accuracy. The purpose of statistical mechanics is not to answer the question: "Starting from some particular information available about the initial conditions of a system, how can we make the best prediction about its future condition?"

The statistical approach allows us to solve problems that cannot be solved at all within the framework of thermodynamics. Moreover, statistical physics provides a rigorous substantiation of the accepted laws of thermodynamics.

In statistical mechanics we do not follow the change in state that would take place in a particular system. Instead, we study the average behaviour of the representative *ensemble* (assembly) of systems of similar structures, and predict what may be expected on an average for the particular system. We, therefore, have to deal, in the realm of statistical mechanics, with groups, variously described as collections, aggregates or populations, rather than with individual or discrete entities; or with the events that happen on an average rather than those that happen on a particular occasion. The theory, thus formulated leads to certain results which are purely macroscopic in content. They are conditioned precisely by the great number of particles, comprising a body, and cease to have meaning when applied to mechanical systems with a smaller number of degrees of freedom.

Originally concerned with elucidating the difficulties of kinetic theory, statistical mechanics is used with great success in diverse branches of physics.

It can explain thermal phenomena in molecular physics, dielectric and magnetic properties in electromagnetic, molecular scattering and thermal radiation in optics and so on.

The theory of statistical mechanics provides a mathematical language for the enunciation and development of physical laws relating to the properties of large assemblies considered as a whole. Unfortunately, the mathematical problem is far too difficult to be solved and the future of the system cannot be determined rigorously. The molecules are present in such large number that the only way of attacking the problem is to apply the laws of probability to their configuration and motion. The application of the theory of probability to the analysis of the motion of large assemblages of microentities is the basis of statistical mechanics and it is in this respect that it differs from classical mechanics.

Since probability arguments are of fundamental significance for the understanding of the behaviour of systems consisting of a large number of particles, it will be useful to review the basic elements of the probability theory. Chapter 2 is devoted to this purpose. While writing this chapter no prior knowledge of probability is assumed. The chapter is purely of an auxiliary nature. Those who are familiar with the basic theory of probability, may skip this chapter, or consider it useful revision.



## BASIC CONCEPTS OF THE THEORY OF PROBABILITY

The theory of probability deals with special laws governing random events.

### 2.1 RANDOM EVENTS

What is a random event?

Suppose we toss a coin. It is impossible to say in advance whether it will show 'heads' or 'tails'. Or suppose, we take a card at random from a deck. Can we say in advance what its suit will be? In each of these examples we carried out an 'experiment' or 'trial', the outcome of which cannot be predicted. A particular event may or may not occur. These are the examples of random events.

Not every event, however, whose result is unknown and does not lend itself to unambiguous prediction may be called random in the sense we have used here. In the two examples we have considered above, the trials were carried out under identical conditions. When we deal with experiments in which the essential circumstances are kept constant and yet repetition of the experiment yields different results, we say the results are random. Consider now a football game played for the World Cup final. Its outcome is uncertain. But it cannot be said to be a random event, since the game is played on different occasions under different conditions. The teams may have new participants; or even the old participants may have acquired new experience and may be in a different state of health, or the games may be played in different countries. Such events are, no doubt, uncertain, but are taken care of by a different theory. Probability theory is concerned with random events.

Although the results of experiments such as those described above cannot be predicted unambiguously, it is possible to determine the *degree of likelihood* — probability — of occurrence of these events.

An elementary understanding of the term 'probability of an event' is inherent in every person with common sense. Probabilities and statistics occupy a major place in our life. We encounter random phenomena in our everyday life and plan our action after estimating the probability of their

occurrence. Some random events are more probable and some are less probable. Laplace, who systematized the theory of probability said:

"The theory of probability at bottom is nothing more than commonsense reduced to calculations."

Thus, although the origin of the theory of probability is more recent, its roots go back to primitive man.

## 2.2 PROBABILITY

To evaluate the probability of a random event, we must first of all, have a unit of measurement. An event is called a 'sure' event if it occurs in an experiment. In the theory of probability, the probability of a sure event is assumed to be equal to 1, and that of an impossible event to be equal to zero. Thus, the probability of a random event  $P(A)$ , lies in the interval zero to one, i.e.

$$0 \leq P(A) \leq 1 \quad \dots(2.1)$$

**Example 2.1** How do we calculate the probability of an event? We shall illustrate the method of calculating probability with the help of a couple of examples.

(i) Suppose a die is cast. What is the probability of appearance of six spots?

(ii) If a coin is tossed, what is the probability that it will show 'heads'?

**Solution.** (i) The die has six faces with spots 1, 2, 3, 4, 5, 6 engraved on them. Casting of the die can yield one of the six results and no other. The total number of possible outcomes of the experiment, thus, is six. If the die is symmetrical, all outcomes are equally likely. It is, therefore, natural to ascribe equal probabilities to each of them. Out of the six possible results only one is favourable for the appearance of six spots. The probability of appearance of six spots, therefore, is  $1/6$ .

(ii) There are only two possible results, 'heads' or 'tails'. Only one of them is favourable for the appearance of 'heads'. The required probability, therefore, is  $\frac{1}{2} = 0.5$ .

Thus, the probability  $P(A)$  of an event A, may be intuitively defined as

$$P(A) = \frac{\text{Number of events favourable for } A}{\text{Total number of possible results}} \quad \dots(2.2)$$

**Example 2.2** What is the probability of pulling from a thoroughly shuffled pack of 52 cards, (i) a queen; (ii) queen of spades?

$$\text{Ans. (i)} \quad \frac{4}{52} = \frac{1}{13}; \quad \text{(ii)} \quad \frac{1}{52}$$

### 2.3 PROBABILITY AND FREQUENCY

In the examples described above all the possible outcomes are assumed to be known. This is not always possible in practice, and, hence, the formula (2.2) is not a general formula. It can be used only in experiments that possess symmetry. Suppose we make the dye asymmetric by adding a little load to one of its faces. Now all the outcomes are not equally likely and we cannot say that the probability of appearance of six spots is  $1/6$ . We must, therefore, adopt another technique for calculating probabilities.

Suppose we cast a die many times, say  $N$  times, and we find that six spots appear  $M$  times. Can we take  $M/N$  as the measure of the probability of appearance of  $N$  spots? Not exactly.

We introduce here a different term to represent the quantity  $M/N$ . We call it frequency of occurrence of the event. We define frequency of an event  $A$ ,  $F(A)$ , as

$$F(A) = \frac{\text{Number of trials in which } A \text{ occurs}}{\text{Total number of trials}} \quad \dots(2.3)$$

Thus, if a coin is tossed 50 time and in 10 of them the coin shows heads, the frequency of this event is  $\frac{10}{50} = 0.2$ . We have seen above that

from the classical definition of probability, the probability of occurrence of heads is 0.5. We see, therefore, that frequency is not the same as probability. But there must be some relation between probability and frequency. The most probable events occur more frequently. This relationship can be found by increasing the number of trials. As the number of trials is increased, the frequency of the event progressively loses its randomness, tends to stabilize and gradually approaches a constant value—the probability of the event. We define probability in terms of frequency as

$$P(A) = \lim_{N \rightarrow \infty} \frac{M}{N} \quad \dots(2.4)$$

One may ask, "how large must  $N$  be, in order to obtain a sufficiently accurate result?" Obviously, trials must be conducted until the ratios  $M/N$  differ from one another by a very small value.

### 2.4 PROBABILITY FROM AN ENSEMBLE

It is not necessary to conduct the trials on the same system. An alternative procedure is to make simultaneous measurements on a large number of identical systems — *an ensemble of systems*. If  $N$  is the total number of systems and a certain event  $A$  occurs in  $M$  of them, the probability of occurrence of  $A$  is  $M/N$ , provided  $N$  is very large. Both methods give identical results.

## 2.5 SOME BASIC RULES OF PROBABILITY THEORY

### 2.5.1 Summation Rule

This is applicable to a set of mutually exclusive events. Two events are said to be mutually exclusive, if the happening of one excludes the possibility of the happening of the other. For example, in a box of volume  $V$ , we select two small non-overlapping regions  $\Delta V_1$  and  $\Delta V_2$  (Fig. 2.1). At a certain instant the presence of a particle in  $\Delta V_1$  rules out the possibility of its being present, at the same instant, in  $\Delta V_2$ , and vice versa. The two events, therefore, are mutually exclusive. We can prove that the probability that one of the two mutually exclusive events occur is equal to the sum of the probabilities of occurrence of each to them.

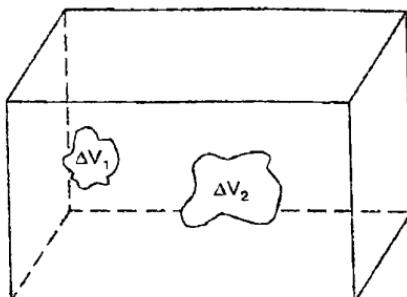


Fig. 2.1

Suppose in  $n$  trials, the particle is found  $m_1$  times in  $\Delta V_1$  and  $m_2$  times in  $\Delta V_2$ . The probabilities of finding the particle in the two regions are respectively.

$$P(\Delta V_1) = \frac{m_1}{n}; \quad P(\Delta V_2) = \frac{m_2}{n} \quad \dots(2.5)$$

What is the probability that the particle will be found in at least one of the two regions? The number of times this happens in  $n$  trials is  $m_1 + m_2$ . Hence the required probability is

$$\begin{aligned} P(\Delta V_1 \text{ or } \Delta V_2) &= \frac{m_1 + m_2}{n} = \frac{m_1}{n} + \frac{m_2}{n} \\ &= P(\Delta V_1) + P(\Delta V_2) \end{aligned} \quad \dots(2.6)$$

We can generalize this summation rule and say: Given any number of mutually exclusive events  $A_1, A_2, \dots$  with probabilities  $P(A_1), P(A_2), \dots$  respectively, the probability that any one of them occurs is the sum of the probabilities of these events, i.e.

$$P(A_1 \text{ or } A_2 \dots) = P(A_1) + P(A_2) + \dots \quad \dots(2.7)$$

Let  $A_1, A_2, \dots, A_N$  be a *complete set* of mutually exclusive events. In  $N$  trials let  $N_1$  be the number of times the event  $A_1$  is realized,  $N_2$  be the number of times  $A_2$  is realized, and so on. Now

$$N_1 + N_2 + \dots + N_n = \sum N_i = N$$

$$\text{Therefore } \frac{N_1}{N} + \frac{N_2}{N} + \dots + \frac{N_n}{N} = \frac{\sum N_i}{N} = 1$$

$$\text{i.e., } P(A_1) + P(A_2) + \dots + P(A_N) = \sum P(A_i) = 1 \quad \dots(2.8)$$

This is known as the *normalization condition* for the probability.

We shall now obtain some useful formulae resulting from the application of the summation rule.

(i) Consider a molecule of a gas moving randomly in a closed metal box. We mentally divide the box into  $n$  identical parallelepipeds, each of volume  $\Delta t$ . Figure 2.2. shows the cross-section of the box. What is the probability that the molecule is in a particular parallelepiped?

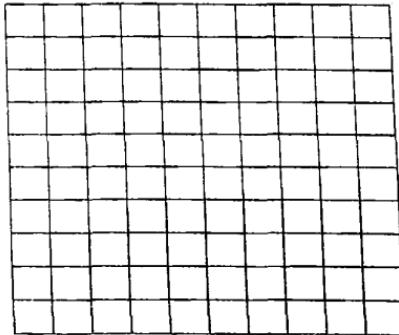


Fig. 2.2

The probability that the molecule is in a definite parallelepiped is the same for all parallelepipeds, say  $P(A)$ . The probability that the molecule is in any one of the parallelepipeds is, by summation rule,  $n P(A)$ . But, this is also the probability that the molecule is in the box which, in fact, is a certainty, i.e., equal to 1.

$$\text{Therefore, } nP(A) = 1 \quad \text{or} \quad P(A) = \frac{1}{n} \quad \dots(2.9)$$

(ii) Consider now a small volume element  $\Delta V$  in the box which includes  $m$  identical parallelepipeds (Fig. 2.3).

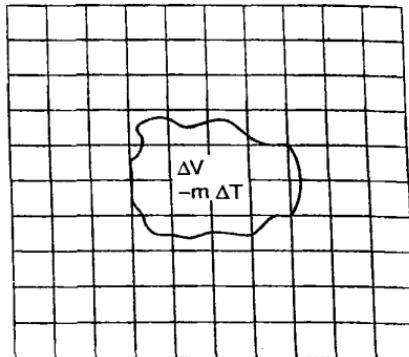


Fig. 2.3

The probability that the molecule is in  $\Delta V$  is, by summation rule,

$$\begin{aligned} P(\Delta V) &= m \times P(A) = \frac{m}{n} \\ &= \frac{m \Delta \tau}{n \Delta \tau} = \frac{\Delta V}{V} \end{aligned} \quad \dots(2.10)$$

We have, thus, expressed the probabilities in terms of volumes.

(iii) Suppose the two regions of volumes  $V_1$  and  $V_2$  in a box of volume  $V$ , overlap as shown in Fig. 2.4. We represent the overlapping region by  $V_{12}$ . What is the probability that the molecule is in the region covered by  $V_1$  and  $V_2$ ? To obtain the volume  $V_T$  of this region, we add  $V_1$  and  $V_2$ , but in doing so, we take  $V_{12}$  twice into account.

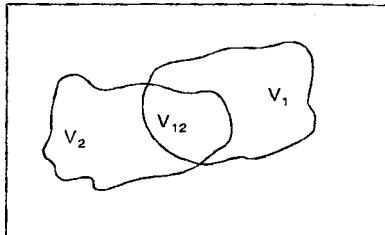


Fig. 2.4

$$\text{Therefore, } V_T = V_1 + V_2 - V_{12} \quad \dots(2.11)$$

Hence, the probability that the molecule is in  $V_T$  is

$$\begin{aligned} P(V_T) &= \frac{V_T}{V} = \frac{V_1 + V_2 - V_{12}}{V} = \frac{V_1}{V} + \frac{V_2}{V} - \frac{V_{12}}{V} \\ &= P(V_1) + P(V_2) - P(V_{12}) \end{aligned} \quad \dots(2.12)$$

where the last term gives the probability that the molecule is in the overlapping region.

Generalizing we can say that if in  $N$  trials,  $N_A$  is the number of times the event  $A$  occurs,  $N_B$  is the number of times the event  $B$  occurs and these numbers also include the number  $N_{AB}$  when both events occur simultaneously, then the total number of events,  $N_{A+B}$  is given by

$$N_{A+B} = N_A + N_B - N_{AB} \quad \dots(2.13)$$

$$\text{Hence, } \frac{N_{A+B}}{N_A + N_B} = \frac{N_A + N_B - N_{AB}}{N} = \frac{N_A}{N} + \frac{N_B}{N} - \frac{N_{AB}}{N}$$

$$\text{i.e., } P(A+B) = P(A) + P(B) - P(AB) \quad \dots(2.14)$$

The last term is the probability of the simultaneous occurrence of events  $A$  and  $B$ .

### 2.5.2 Corollary

If the probability of occurrence of an event  $A$  is  $P(A)$  and that of its non-occurrence  $p(\bar{A})$ ;

then  $P(A) + p(\bar{A}) = 1$  ... (2.15)

It is sometimes easier to calculate the probability  $p(\bar{A})$  than to calculate  $P(A)$ . In such cases  $P(A)$  can be found from

$$P(A) = 1 - P(\bar{A}) \quad \dots(2.16)$$

### 2.5.3 Multiplication Rule: Joint Probability

In the calculation of probabilities we sometimes come across random events, such that the probability of occurrence of one does not affect the probability of occurrence of the other. For example, in Fig. 2.1, the probability that a molecule  $A$  gets into  $\Delta V_1$  at a particular instant is

$P_1 = \frac{\Delta V_1}{V}$ . The probability that another molecule  $B$  gets into  $\Delta V_2$  at the

same instant is  $P_2 = \frac{\Delta V_2}{V}$ , regardless of whether or not the molecule  $A$  gets into  $\Delta V_1$ . Such events are said to be *statistically independent* or *uncorrelated*.

What is the probability of joint occurrence of these events, i.e., the probability of  $A$  getting into  $\Delta V_1$  and  $B$  getting into  $\Delta V_2$  at the same instant?

Suppose in  $N$  trials the molecule  $A$  is found  $m$  times in  $\Delta V_1$ . If  $P_2$  is the probability that  $B$  gets into  $\Delta V_2$ , irrespective of the presence of  $A$  in  $\Delta V_1$ , the number of times the two events will occur simultaneously is  $mP_2$ . The joint probability of occurrence of these two events, therefore, is

$$\frac{mP_2}{N} = \frac{m}{N} \times P_2 = P_1 \cdot P_2$$

because  $P_1 = \frac{m}{N}$  ... (2.17)

Thus, probability of joint occurrence of two independent events is equal to the product of the probabilities of each of the independent events.

**Example 2.3** We throw a die twice, and obtain two numbers. What is the probability that these numbers are 6 and 4 precisely in that order?

**Solution.** The probability that the first throw gives a 6 is  $1/6$ . The probability that the second throw gives a 4 is also  $1/6$ . These two events are independent. Therefore, the required probability is

$$\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$$

**Example 2.4** What is the probability that a deuce and ace appear when two dice are thrown?

**Solution.** The probability that the first die shows a deuce is 1/6 and the probability that the second one shows an ace is also 1/6. The two events being independent, the probability of the joint event is 1/36. There is yet another alternative for this joint event to occur, when the first die gives an ace and the second one gives a deuce. The probability of such a joint event is again 1/36. These two alternatives are mutually exclusive. Therefore, the required probability is

$$\frac{1}{36} + \frac{1}{36} = \frac{1}{18}$$

✓ **Example 2.5** Five marksmen shoot simultaneously at a target and the probability for each of them to hit the target is 1/3. What is the probability for at least one marksman hitting the target?

**Solution.** The probability for each marksman missing the target is  $1 - 1/3 = 2/3$ . The probability for all five marksmen missing the target is  $(2/3)^5$ . Therefore, the probability for at least one marksman hitting the target is

$$1 - \left(\frac{2}{3}\right)^5 = 0.87$$

We have used here the relation (2.16).

#### 2.5.4 Conditional Probability

The probability for an event  $A$  to occur under the condition that event  $B$  has occurred is called the *conditional probability* of the occurrence of event  $A$  and is denoted by  $P(A/B)$ .

In the case of the overlapping regions in Fig. 2.4, what is the probability of finding a molecule in the region  $V_1$  when it is contained in  $V_2$ ? This amounts to calculating the probability of finding the molecule in the region  $V_{12}$  when it is contained in  $V_2$ . One can see that this is given by

$$P(V_1/V_2) = \frac{V_{12}}{V_1} \quad \dots(2.18)$$

In the same way in the case of the generalization discussed in case (iii), the probability for the event  $A$  to occur under the condition that the event  $B$  has occurred is

$$P(A/B) = \frac{N_{AB}}{N_B} \quad \dots(2.19)$$

Dividing the numerator and the denominator by  $N$ , the total number of trials, we have

$$P(A/B) = \frac{N_{AB}/N}{N_B/N} = \frac{P(AB)}{P(B)} \quad \dots(2.20)$$

Similarly

$$P(B/A) = \frac{P(AB)}{P(A)} \quad \dots(2.21)$$

It may be noted that in general these two results are not equal.

From Eqs. (2.20) and (2.21), we get

$$P(AB) = P(A/B)P(B) = P(B/A)P(A) \quad \dots(2.22)$$

**Example 2.6** An urn contains 4 black and 3 white balls. What is the probability that on two successive draws, the balls drawn are both black?

**Solution.** Let the event that the first ball drawn is black be denoted by A. Its probability is  $P(A) = 4/7$ . This event is followed by the second event B, in which the second ball drawn is also black. Now if the event A is realized the number of balls is reduced by one. The second ball, therefore, is selected from 6 balls of which 3 are black. Hence, the probability for the event B under the condition that A is realized is  $P(B/A) = \frac{3}{6} = \frac{1}{2}$ . The first event thus, affects the probability of the second event. The probability of the composite event  $A + B$  is

$$P(A + B) = P(A) \cdot P(B/A) = \frac{4}{7} \times \frac{1}{2} = \frac{2}{7}$$

**Example 2.7** In a box there are 10 cut up alphabet cards with the letters 3A's, 4M's and 3N's. We draw three cards one after another and place these on the table in the order they have been drawn. What is the probability that the word 'MAN' will appear?

**Solution.** The probability that the first card is M, is 4/10. The probability that the second letter is A, subject to the realization of the first condition is 3/9. Similarly, the probability for the third letter to be N is 3/8. Hence

$$P(MAN) = \frac{4}{10} \cdot \frac{3}{9} \cdot \frac{3}{8} = \frac{1}{20}$$

**Example 2.8** In the preceding example suppose the letters are drawn out simultaneously. What is the probability that the word 'MAN' can be obtained from the drawn letters?

**Solution.** In this case we have altered the conditions of drawing the events. In the preceding example, the cards were to be drawn in the order  $M \rightarrow A \rightarrow N$ . But now the order does not matter. It can be MAN, NAM, AMN, ...., etc., there being six (3!) such variants. We have to calculate the probabilities of these six alternatives and these being mutually

exclusive, we have to add up these probabilities to find the required probability. Thus

$$P(\text{AMN}) = \frac{3}{10} \cdot \frac{4}{9} \cdot \frac{3}{8} = \frac{1}{20}$$

$$P(\text{NAM}) = \frac{3}{10} \cdot \frac{3}{9} \cdot \frac{4}{8} = \frac{1}{20}$$

$$P(\text{MNA}) = \frac{4}{10} \cdot \frac{3}{9} \cdot \frac{3}{8} = \frac{1}{20}, \text{ etc.}$$

The required probability is  $6 \times \frac{1}{20} = \frac{3}{10}$

## 2.6 CONTINUOUS RANDOM VARIABLES

In our discussion so far we have considered only discrete random variables, that is, the variables that take on values differing from one another by a finite value. There are other kinds of variables which take on a continuous series of values and, hence are continuous random variables. For example, the height of rising water during a spate varies continuously. In Fig. 2.5 we have shown a cubical vessel with side  $a$  containing a molecule which moves randomly. The  $z$  coordinate of the molecule may take values from  $z = 0$  to  $z = a$ . It is senseless to talk about the probability that a continuous variable has a given value.

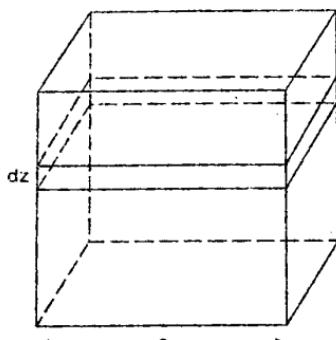


Fig. 2.5

We can only talk about the probability of such variables akin to a certain value within a certain interval. In the case of the cubical vessel, we can find the probability that the variable takes on values between  $z$  and  $z + dz$ . Naturally, the probability must be proportional to  $dz$ . Smaller the interval  $dz$ , lesser is the chance of the molecule being found in  $dz$ . We can, therefore, write

$$P(dz) = f(z) dz \quad \dots(2.23)$$

where  $f(z)$  is a function of  $z$  and is called the *probability density*. In general, the probability that a molecule is found in the volume element  $\Delta V$  is

$$P(\Delta V) = f(x, y, z) \Delta V \quad \dots(2.24)$$

**Example 2.9** What is the probability that a molecule in the cubical vessel (Fig. 2.5) lies in the volume  $\Delta V$  formed by two planes at  $z$  and  $z + dz$ ?

**Solution.** The volume of the vessel is  $V = a^3$ . The volume of the element  $\Delta V = a^2 dz$ .

$$\text{Therefore } P(\Delta V) = \frac{\Delta V}{V} = \frac{a^2 dz}{a^3} = \frac{1}{a} dz$$

The probability density in this case is  $1/a$ , whose dimension is the reciprocal of the length. This is in keeping with our expectation, since probability is a dimensionless quantity. What was not expected is that it should be a constant, since we have defined probability as a function of coordinates. It is a constant in this particular example, because the vessel has a cubical shape and all positions of the molecule in it are equally possible.

**Example 2.10** Find the probability that a certain molecule lies in a volume element  $\Delta V$  formed by the planes at  $z$  and  $z + dz$ , in a conical vessel whose height is  $H$  and the radius of the base is  $R$  (Fig. 2.6). The volume of the vessel is

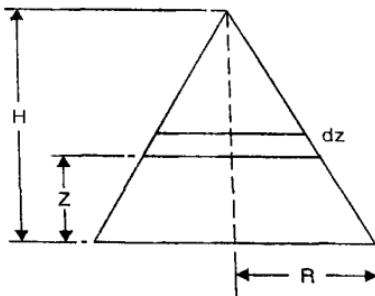


Fig. 2.6

$$V = \frac{1}{3} \pi R^2 H$$

**Solution.** The volume  $\Delta V$  is given by

$$\Delta V = \pi r^2 dz$$

where  $r$  is the radius of the base of the element.

$$\text{Now } \frac{r}{R} = \frac{H - z}{H}$$

$$\text{Therefore } r = \frac{R(H - z)}{H}$$

$$\text{and } \Delta V = \pi \frac{R^2 (H - z)^2}{H^2} dz$$

$$\text{Hence } P(\Delta V) = \frac{\Delta V}{V} = \frac{\pi R^2 (Hz)^2 dz}{H^2} \cdot \frac{3}{\pi R^2 H} = \frac{3(H - z)^2}{H^3} dz$$

## 2.7 PROBABILITY FOR A MOLECULE TO LIE IN A FINITE VOLUME

Suppose in a total number of observations  $N_o$ , the molecule was found in a small volume element  $dV$  in  $dN$  observations. The probability that the molecule lies in  $dV$  is

$$P(dV) = \frac{dN}{N_o}$$

$$\text{Therefore } dN = N_o P(dV) = N_o f(x, y, z) dV \quad \dots(2.25)$$

where we have used Eq. (2.24).

In a finite volume  $V$ , the number of molecules will be

$$N(V) = N_o \int_V f(x, y, z) dV$$

The probability that a molecule lies in the volume  $V$  is

$$P(V) = \frac{N(V)}{N_o} = \int_V f(x, y, z) dV \quad \dots(2.26)$$

Thus, knowing the probability density in a certain region, the probability of appearance of a molecule in this region can be calculated using Eq. (2.26).

The following relation needs no explanation

$$\int_{V \rightarrow \infty} f(x, y, z) dV = 1 \quad \dots(2.27)$$

## 2.8 MEAN VALUE OF A DISCRETE RANDOM VARIABLE

In statistical physics, to get an overall picture, we are sometimes interested in the *mean value* of a random variable, which is also known as *mathematical expectation*. This is the central value of the variable about which its various values are distributed.

Suppose we are interested in the number of molecules in a volume element  $\Delta V$  in a closed vessel having a volume  $V$ . We carry out a large number of trials, say  $M$ . In these, suppose we register  $m_1$  times the value  $n_1$ ,  $m_2$  times the value  $n_2$  and so on. The mean value is then defined as

$$\begin{aligned} n &= \frac{m_1 n_1 + m_2 n_2 + \dots}{m_1 + m_2 + \dots} = \frac{m_1 n_1 + m_2 n_2 + \dots}{M} \\ &= \frac{m_1}{M} n_1 + \frac{m_2}{M} n_2 + \dots = P(n_1) n_1 + P(n_2) n_2 + \dots \\ &= \sum_{i=1}^M P(\bar{n}_i) (n_i) \end{aligned} \quad \dots(2.28)$$

The specification of the probabilities of all  $n_i$  values, gives complete statistical description of the system.

In general, if  $f(n_i)$  is any function of  $n_i$ , the mean value of  $f(n_i)$  is given by

$$\langle f(n_i) \rangle = \sum_i P(n_i) f(n_i) \quad \dots(2.29)$$

## 2.9 MEAN VALUE OF A CONTINUOUS RANDOM VARIABLE .

For a continuous variable  $z$ , the probability that it takes values in the range from  $z$  to  $z + dz$  is by definition

$$P(z) = f(z) dz$$

where  $f(z)$  is the probability density. Hence the mean value of  $z$  is given by

$$\langle z \rangle = \sum P(z) z = \int z f(z) dz \quad \dots(2.30)$$

where the integral is evaluated over all possible values of  $z$ . The mean value of a function  $\phi(z)$  is

$$\langle \phi(z) \rangle = \int \phi(z) f(z) dz \quad \dots(2.31)$$

It must be mentioned here that the mean value depends on the variable, over which the averaging is carried out.

**Example 2.11** Find the mean distance of a material point moving along a semicircle from its diameter by averaging it (a) along the semicircle; (b) along the projection of the point on the diameter of the circle.

**Solution.** Let  $R$  be the radius of the circle (Fig. 2.7). Suppose in a time  $t$  the point has moved through a small distance  $s$  along the semicircle. Now the distance of the point from the diameter is

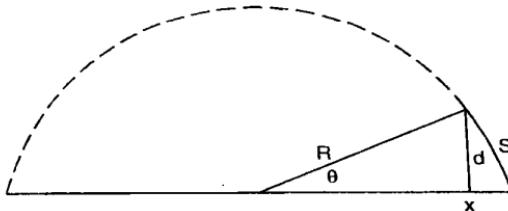


Fig. 2.7

$$d = R \sin \theta = R \sin \left( \frac{s}{R} \right)$$

$$\text{Therefore, (a)} \quad \langle d \rangle_s = \frac{1}{\pi R} \int_0^{\pi R} R \sin \left( \frac{s}{R} \right) ds = \frac{2R}{\pi}$$

and (b) since  $d = \sqrt{R^2 - x^2}$

$$\begin{aligned}\langle d \rangle_x &= \frac{1}{2R} \int_{-R}^R \sqrt{R^2 - x^2} dx \\ &= \frac{\pi R}{4}\end{aligned}$$

## 2.10 VARIANCE : DISPERSION

Sometimes it is convenient and even necessary to measure the possible values of a variable with respect to its mean value. We may as well be interested in knowing how the values are dispersed about the mean value. The deviation of a variable  $n$  from its mean value is

$$\Delta n = n - \langle n \rangle$$

If we decide to find the mean of the deviation to obtain an overall picture of the spread of the values, we get

$$\langle \Delta n \rangle = \langle n - \langle n \rangle \rangle = \langle n \rangle - \langle n \rangle = 0$$

Mean deviation, therefore, does not serve our purpose as it does not give us the measure we are seeking. Hence, we have to use a different parameter. This parameter is the mean square deviation of the variable from its mean value. It is called *Variance* or *dispersion* or "the second moment of  $n$  about its mean", and is denoted by  $\sigma$ .

$$\text{Thus } \sigma^2 = \langle (n - \langle n \rangle)^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2 \quad \dots(2.32)$$

This determines the degree of scattering of a random variable and is, in a way, a measure of randomness.

We can easily show that for discrete variable  $n$

$$\begin{aligned}\sigma^2 &= \langle (\Delta n)^2 \rangle = \sum P(n) (\Delta n)^2 \\ &= \sum P(n) (n - \langle n \rangle)^2\end{aligned} \quad \dots(2.33)$$

and for a continuous variable

$$\sigma^2 = \int_{-\infty}^{\infty} P(n) (n - \langle n \rangle)^2 dn \quad \dots(2.34)$$

The standard deviation or the root mean square deviation  $\sigma$  is given by the square root of variance, i.e.

$$\sigma = \left\{ \langle n^2 \rangle - \langle n \rangle^2 \right\}^{1/2} \quad \dots(2.35)$$

## 2.11 PROBABILITY DISTRIBUTION

In the examples discussed so far we have assumed uniform distribution. Thus, in a uniform distribution of space we assume that each region of the space is equally probable. In some situation, however, the physical laws governing the system cause some regions of the space to be more probable than others. This is indicated by a weight function  $W(x)$  which varies with  $x$ . Suppose a particle can move freely along a line of length  $L$ , what is the probability that it lies within a small element  $dx$  at  $x$ ? In the case of uniform distribution, this would have been  $dx/L$ . If, however, there is a non-uniformity in the distribution, we write

$$P(x) dx = W(x) \frac{dx}{L} \quad \dots(2.36)$$

where  $W(x)$  gives the weightage of the region. The normalization condition gives

$$\int_0^L P(x) dx = 1 \quad \dots(2.37)$$

Frequently, a distribution function is introduced rather than a weight function. Suppose,  $N$  particles are distributed over a line of length  $L$  according to a certain distribution law  $f(x)$ . Then, the number of particles in the interval between  $x$  and  $x + dx$  is  $f(x) dx$ . Obviously

$$\int_0^L f(x) dx = N \quad \dots(2.38)$$

From Eqs. (2.37) and (2.38), we get

$$f(x) = NP(x). \quad \dots(2.39)$$

**Example 2.12** One thousand particles are distributed along a line of length 1 m; with a distribution function  $f(x) = Bx\left(1 - \frac{x}{L}\right)$ , where  $L$  is the length of the line. How many particles lie between  $x$  and  $x + dx$ , where  $dx = 1 \text{ mm}$ ?

**Solution.** The required number is

$$n = f(x) dx = Bx\left(1 - \frac{x}{L}\right) dx.$$

From the normalization condition

$$\int_0^L Bx\left(1 - \frac{x}{L}\right) dx = N = 1000$$

i.e.,

$$\frac{BL^2}{6} = 1000$$

Therefore,  $B = 6000$  (because  $L = 1$ )

$$\begin{aligned}\text{Hence, } n &= 6000 (x - x^2) \times 0.001 \\ &= 6(x - x^2)\end{aligned}$$

In a given experiment a stochastic (random) variable  $x$  may have any one of a number of values  $x_1, x_2, \dots$ . Each one of these will appear with a certain probability  $f(x)$ . The complete set of values  $f(x_i)$  is called the *probability distribution*. The values  $f(x_i)$  must satisfy the condition

$$f(x_i) \geq 0$$

$$\sum_i f(x_i) = 1 \quad \dots(2.40)$$

where the sum is taken over all values of the variable  $x$ . All possible information about the variable  $x$  can be found if the distribution  $f(x_i)$  is known.

## 2.12 BINOMIAL DISTRIBUTION

Suppose we carry out a series of experiments in which each experiment has only two possible outcomes. For example, experiments to evaluate the magnetic moment of a system of electrons which have spins

$\frac{1}{2}$  or  $-\frac{1}{2}$ , or the traditionally known experiment of tossing coins in

which either 'heads' or 'tails' appear. Let the probability of appearance of 'heads' be represented by  $p$  and that of 'tails' by  $q$ , where

$$p + q = 1 \quad \dots(2.41)$$

We list below in a tabular form (Table 2.1), the outcome of coin-tossing. In column (1) we give the number of coins tossed; in column (2) the possible outcomes (head or tails); in column (3), probability of their occurrence and in column (4) we have entered the probability terms disregarding the order of  $H$  (head) or  $T$  (tail) and considering only number.

Table 2.1

(1) Number of coins	(2) Possible outcomes	(3) Probability	(4)
1	$H, T$	$p, q$	$p, q$
2	$HH, HT$ $TH, TT$	$pp, pq$ $qp, qq$	$p^2, 2pq, q^2$
3	$HHH, HHT$ $HTH, THH,$ $TTH, THT,$ $HTT, TTT$	$ppp, ppq,$ $pqp, qpp,$ $qqp, qpq$ $pqq, qqq$	$p^3, 3p^2 q$ $3pq^2, q^3$

One can easily recognize that the terms in the last column are the terms of the algebraic expansion of  $(p + q)^1$  for  $n = 1$ ;  $(p + q)^2$  for  $n = 2$  and  $(p + q)^3$  for  $n = 3$ , respectively. It is, therefore, possible to conjecture that the situation for  $n$  coins will be symbolized by the terms of

$$(p + q)^n = q^n + \frac{n}{1!} pq^{n-1} + \frac{n(n-1)}{2!} p^2 q^{n-2} + \dots + p^n \quad \dots(2.42)$$

Because of its analogy with the binomial theorem, the distribution given in the last column of Table 2.1 is called *binomial distribution*.

Let us now consider a more general case of a series of experiments, in which each experiment has only two possible outcomes, say  $A$  and  $\bar{A}$ , with probabilities  $p$  and  $q : p + q = 1$ . Suppose in  $N$  trials, the outcome  $A$  results  $n$  times and  $\bar{A}$ ,  $n'$  times. Then

$$N = n + n' \quad \dots(2.43)$$

Since  $N$  trials are statistically independent, the probability of such a result is  $p^n q^{n'}$ . But a situation in which  $A$  results  $n$  times and  $\bar{A}$ ,  $n'$  times can be achieved in many alternative ways. Let the member of distinct ways in which the above result is obtained be  $C(n)$ . The probability, therefore, is

$$P(n) = C(n) p^n q^{n'} \quad \dots(2.44)$$

Suppose, for example, in 4 trials,  $A$  results 3 times and  $\bar{A}$  once. The number of ways in which this situation is achieved is  $4! = \frac{4!}{3!1!}$ , shown in Table 2.2.

Table 2.2

1	2	3	4	5
A	A	A	A	1
A	A	A	A	2
A	A	A	A	3
A	A	A	A	4

In general the number of distinct ways, in which  $A$  results  $n$  times and  $\bar{A}$  in  $n'$  times in  $N$  trials, is given by

$$C_N(n) = \frac{N!}{n!n'^!} = \frac{N!}{n!(N-n)!} \quad \dots(2.45)$$

The required probability, therefore, is

$$P(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n} \quad \dots(2.46)$$

Consider now the binomial expansion of  $(p + q)^N$

$$(p + q)^N = q^N + Npq^N + \frac{N(N-1)}{2!} p^2 q^{N-2} + \dots$$

$$= \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n} \quad \dots(2.47)$$

Comparison of Eqs. (2.46) and (2.47) shows that each term of the binomial expansion gives the probability  $P(n)$ . One can easily see that the probabilities thus obtained satisfy the normalization condition.

$$\sum P(n) = \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n} = \sum (p+q)^N = 1 \quad \dots(2.48)$$

(because  $p + q = 1$ )

**Example 2.13** A vessel of volume  $V$  is mentally divided into two equal parts. The vessel contains six molecules. Obtain the probability distribution for the molecules to lie in the half of the box.

**Solution.** The probability that a molecule is found in the left half is obviously  $1/2$ , i.e.,

$$p = q = \frac{1}{2}.$$

From Eq. (2.46) the probability for the absence of molecules ( $n = 0$ ) or for all the molecules ( $n = 6$ ) to be found in the left half is  $1/64$ . The probability for one molecule to lie in the left half and five in the right or vice versa is 6. The probability for the absence of molecules ( $n = 0$ ) or for all the molecules ( $n = 6$ ) to be found in the left half is  $1/64$ . The probability for one molecule to lie in the left half and five in the right or vice versa is  $6/64$ . The probability for 2 molecules in the left half and 4 in the right or vice versa is  $15/64$  and the probability for 3 molecules in each half is  $20/64$ . The distribution is shown graphically in Fig. 2.8. The event of greatest probability is when the number of molecules is the same in both halves. Hence, the molecules in the vessel will move about until on the average there will be an approximately equal number of molecules in each half of the vessel.

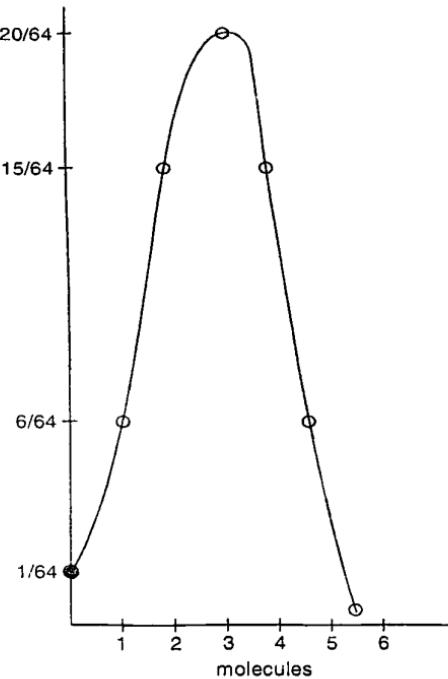


Fig. 2.8

## 2.13 MEAN VALUE WHEN THE DISTRIBUTION IS BINOMIAL

Then mean value of a variable  $n$  is given by

$$\langle n \rangle = \sum_{n=0}^N n P(n)$$

In the case of a binomial distribution, this becomes

$$\begin{aligned}\langle n \rangle &= \sum_{n=0}^N \frac{n N!}{n!(N-n)!} p^n q^{N-n} \\ &= \sum_{n=0}^N \frac{N!}{n!(N-n)!} \left( p \frac{\partial p^n}{\partial p} \right) q^{N-n} \\ &= p \frac{\partial}{\partial p} \left\{ \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n} \right\} \\ &= p \frac{\partial}{\partial p} \sum P(n) \\ &= p \frac{\partial}{\partial p} (p+q)^N\end{aligned}$$

where we have used Eq. (2.47).

$$\text{Therefore } \langle n \rangle = pN(p+q)^{N-1} = pN$$

(because  $p+q=1$ ) ... (2.49)

## 2.14 FLUCTUATIONS

Although the mean obtained in Eq. (2.49) is generally close to the experimental value, chaotic deviations from the mean value, known as *fluctuations*, sometimes become significant. The measure of these fluctuations is the standard deviation

$$\sigma^2 = \langle n^2 \rangle - \langle n \rangle^2$$

In the case of the binomial distribution

$$\begin{aligned}\langle n^2 \rangle &= \sum_{n=0}^N \frac{n^2 N!}{n!(N-n)!} p^n q^{N-n} \\ &= \sum_{n=0}^N \frac{N!}{n!(N-n)!} \left( p \frac{\partial}{\partial p} \right) \left( p \frac{\partial}{\partial p} \right) p^n q^{N-n}\end{aligned}$$

$$\begin{aligned}
 &= \left( p \frac{\partial}{\partial p} \right) \left( p \frac{\partial}{\partial p} \right) \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n} \\
 &= \left( p \frac{\partial}{\partial p} \right) \left( p \frac{\partial}{\partial p} \right) (p+q)^N \\
 &= p [N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2}] \\
 &= pN + p^2 N(N-1) = pN - p^2 N + p^2 N^2 \\
 &= pN(1-p) + p^2 N^2 = Npq + p^2 N^2
 \end{aligned}$$

Hence,

$$\begin{aligned}
 \sigma^2 &= \langle n^2 \rangle - \langle n \rangle^2 = Npq + p^2 N^2 - p^2 N^2 \\
 &= Npq
 \end{aligned} \quad \dots(2.50)$$

The root mean square deviation is

$$\sigma = \sqrt{Npq} \quad \dots(2.51)$$

The fractional deviation is given by

$$\frac{\sigma}{\langle n \rangle} = \frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{Np}} \quad \dots(2.52)$$

This relation shows that larger the value of  $N$ , smaller is the fractional deviation, i.e., sharper the peak or smaller the width of the distribution.

**Example 2.14** Consider a binomial distribution for a system for which  $p = \frac{1}{3}$ ,  $q = \frac{2}{3}$ ,  $N = 6$ . Determine the standard deviation and find the probability that  $n$  is in the range  $\langle n \rangle - \sigma$  to  $\langle n \rangle + \sigma$ .

**Solution.** Here,  $\langle n \rangle = pN = 2$ ;  $\sigma^2 = Npq = \frac{4}{3}$ , i.e.,  $\sigma = \frac{2}{\sqrt{3}} \approx 1$

Therefore,  $\langle n \rangle - \sigma \approx 1$  and  $\langle n \rangle + \sigma \approx 3$ .

The values of  $n$  that lie in this range are 1, 2 and 3. Probabilities for these values calculated using Eq. (2.46) are 0.263, 0.329 and 0.219, respectively.

Therefore, the probability that  $n$  lies in the range  $\langle n \rangle - \sigma$  to  $\langle n \rangle + \sigma$  is  $0.263 + 0.320 + 0.219 = 0.811$ .

## 2.15 STIRLING APPROXIMATION

The calculation of probability  $p(n)$  in the case of a binomial distribution becomes laborious, because it involves the computation of factorials of large numbers, sometimes as large as  $10^{19}$ . It is, therefore,

desirable to have a formula for rapidly assessing the values of factorials of such numbers. Such a formula was provided by Stirling.

Since  $N = 1, 2, 3, \dots N$

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \dots \ln N = \sum_{n=1}^N \ln n \quad \dots(2.53)$$

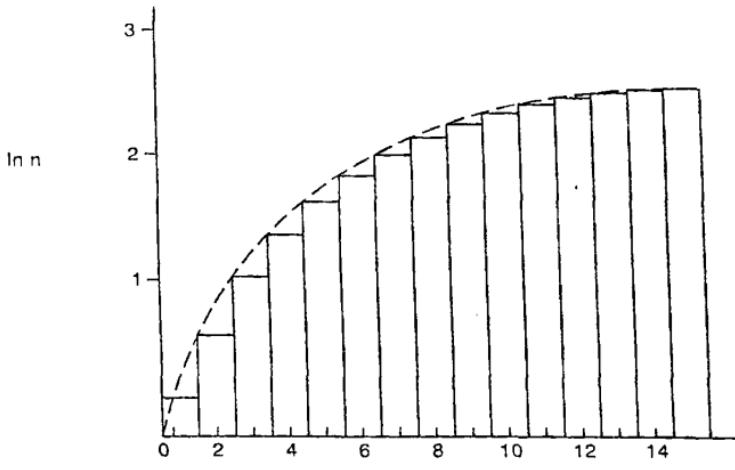


Fig. 2.9

In Fig. 2.9 the values of  $\ln n$  against  $n$  have been plotted. The required sum  $\sum \ln (n)$  is given by the area  $S$  confined by the stepped line and the axis of abscissa. In the same figure we have plotted  $\ln x$  against  $x$  (dashed curve), where  $x$  is assumed to be a continuous variable. The area under the dashed curve is given by

$$\begin{aligned} S' &= \int_1^N \ln x \, dx = [x \ln x]_1^N - \int_1^N dx \\ &= N \ln N - N + 1 \end{aligned}$$

For large  $N$  we can assume  $S = S'$

$$\text{Therefore } \ln N! = \sum_{n=1}^N \ln n = N \ln N - N + 1 \quad \dots(2.54)$$

$$\text{If } N \text{ is very large, } \ln N! = N \ln N - N \quad \dots(2.55)$$

A more rigorous derivation yields

$$N! = \sqrt{2\pi N} \left(\frac{N}{e}\right)^N \quad \dots(2.56)$$

## 2.16 POISSON DISTRIBUTION

There are two limiting forms of the binomial distribution which are very useful in statistical physics. One of them is known as *Poisson distribution*. This distribution is valid when

- (i)  $N$  is very large,  $N > > 1$
- (ii)  $p$  is very small,  $p < < 1$
- (iii)  $n$  is very small,  $n < < N$

but  $np$  is finite; that is, we assume that values of  $n$  have such a low probability that it may be ignored.

Using these conditions we can approximate the factors appearing in the binomial distribution. Thus

$$\begin{aligned} \frac{N!}{(N-n)!} &= N(N-1)\dots(N-n+1) \\ &\approx N^n \end{aligned} \quad \dots(2.57)$$

Here, because of the condition (i), we have assumed each factor equal to  $N$ .

$$\text{Now, } q = 1 - p$$

$$\text{therefore, } \ln q = \ln(1-p)$$

Expanding the right hand side by Taylor's theorem and retaining only the first term (because  $p$  is very small), we get

$$\ln q = -p \text{ i.e., } q = e^{-p}$$

$$\text{Hence, } q^{N-n} = e^{-p(N-n)} \approx e^{-pN} \quad \dots(2.58)$$

With these approximations the binomial distribution takes the form

$$P(n) = \frac{N^n}{n!} p^n e^{-pN} = \frac{(pN)^n}{n!} e^{-pN} \quad \dots(2.59)$$

This is known as the *Poisson distribution*. It still contains the term  $n!$ ; but since  $n$  is very small, it can easily be evaluated. We can write the Poisson distribution in the form

$$P(n) = \frac{\langle n \rangle^n}{n!} e^{-\langle n \rangle} \quad \dots(2.60)$$

where we have used Eq. (2.49). From this relation we see that

$$\sum P(n) = \sum \frac{\langle n \rangle^n}{n!} e^{-\langle n \rangle} = e^{\langle n \rangle} \cdot e^{-\langle n \rangle} = 1 \quad \dots(2.61)$$

$$\left( \text{because } \sum \frac{\langle n \rangle^n}{n!} = e^{\langle n \rangle} \right)$$

The Poisson distribution, therefore, is a properly normalized probability distribution.

## 2.17 MEAN VALUES AND STANDARD DEVIATION IN THE CASE OF POISSON DISTRIBUTION

$$\begin{aligned}
 \langle n \rangle &= \sum_{n=0}^{\infty} n P(n) = \sum_{n=0}^{\infty} n \frac{\langle n \rangle^n}{n!} e^{-\langle n \rangle} \\
 &= \langle n \rangle e^{-\langle n \rangle} \sum_{n=1}^{\infty} \frac{\langle n \rangle^{n-1}}{(n-1)!} \\
 &= \langle n \rangle e^{-\langle n \rangle} e^{\langle n \rangle} = \langle n \rangle = pN
 \end{aligned} \quad \dots(2.62)$$

Thus, Poisson distribution has the same mean value as the binomial distribution.

$$\begin{aligned}
 \text{Now, } \langle n^2 \rangle &= \sum_{n=0}^{\infty} \frac{n^2 \langle n \rangle^n}{n!} e^{-\langle n \rangle} \\
 &= \sum_{n=0}^{\infty} \frac{[n(n-1)+n]}{n!} \langle n \rangle^n e^{-\langle n \rangle} \\
 &= \sum_{n=2}^{\infty} \frac{\langle n \rangle^n}{(n-2)!} e^{-\langle n \rangle} + \sum_{n=1}^{\infty} \frac{\langle n \rangle^n}{(n-1)!} e^{-\langle n \rangle} \\
 &= \langle n \rangle^2 \sum_{n=2}^{\infty} \frac{\langle n \rangle^{n-2}}{(n-2)!} e^{-\langle n \rangle} + \langle n \rangle \sum_{n=1}^{\infty} \frac{\langle n \rangle^{n-1}}{(n-1)!} e^{-\langle n \rangle} \\
 &= \langle n \rangle^2 e^{\langle n \rangle} e^{-\langle n \rangle} + \langle n \rangle e^{\langle n \rangle} e^{-\langle n \rangle} \\
 &= \langle n \rangle^2 + \langle n \rangle
 \end{aligned} \quad \dots(2.63)$$

$$\text{Therefore, } \sigma^2 = \langle n^2 \rangle - \langle n \rangle^2 = \langle n \rangle^2 + \langle n \rangle - \langle n \rangle^2 = \langle n \rangle \quad \dots(2.64)$$

$$\text{and } \sigma = \langle n \rangle^{1/2} \quad \dots(2.65)$$

$$\frac{\sigma}{\langle n \rangle} = \frac{\langle n \rangle^{1/2}}{\langle n \rangle} = \langle n \rangle^{-1/2} \quad \dots(2.66)$$

Some of the physical systems which can be described by the Poisson distribution are: number of electrons from a thermionic cathode, radioactive emission, etc.

## 2.18 GAUSSIAN DISTRIBUTION

The other limiting form of the binomial distribution is the Gaussian distribution which, perhaps, is the most important distribution in statistical

mechanics. This distribution becomes valid when  $N$  is large and  $n$  also is large but not too close to  $N$ .

It can be shown that the binomial distribution

$$P(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n} \quad \dots(2.67)$$

tends to exhibit a maximum which is very much pronounced when  $N$  is large.

For large values of  $n$ , the change in  $P(n)$ , when  $n$  changes by unity, is very small. We can, therefore, treat  $P(n)$  as a slowly varying function of continuous variable  $n$ . We shall deal here with  $\ln P(n)$ , since it is a much more slowly varying function of  $n$ :

$$\begin{aligned} \ln P(n) &= \ln \left( \frac{N!}{n!(N-n)!} p^n q^{N-n} \right) \\ &= \ln N! - \ln n! - \ln (N-n)! + n \ln p + (N-n) \ln q \end{aligned}$$

Using Stirling's formula

$$\begin{aligned} \ln P(n) &= N \ln N - N - n \ln n + n - (N-n) \ln (N-n) \\ &\quad + N - n + n \ln p + (N-n) \ln q \\ &= N \ln N - n \ln n - (N-n) \ln (N-n) + n \ln p \\ &\quad + (N-n) \ln q \end{aligned}$$

Differentiating with respect to  $n$

$$\begin{aligned} \frac{d}{dn} \ln P(n) &= -\ln n - 1 + \ln (N-n) + 1 + \ln p - \ln q \\ &= \ln \frac{(N-n)p}{nq} \end{aligned} \quad \dots(2.68)$$

For  $P(n)$  to be maximum

$$\ln \frac{(N-n)p}{nq} = 0; \text{ i.e., } \frac{(N-n)p^e}{nq} = 1 \quad \dots(2.69)$$

$$\text{or } \frac{(N-n)p}{n(1-p)} = 1, \text{ i.e., } n = Np \quad \dots(2.70)$$

Therefore,  $P(n)$  reaches maximum at the most probable value of  $n = Np = \langle n \rangle$ . The probability  $P(n)$ , thus, is quite large in the neighbourhood of the value  $\langle n \rangle$  of  $n$  and becomes negligible when  $n$  differs much from  $\langle n \rangle$ . The domain of interest, therefore, is that in which  $P(n)$  is not negligible. We will obtain a probability distribution that is valid in this region.

Let us investigate the behaviour of  $P(n)$  near its maximum value.

Assuming  $n - \langle n \rangle$  to be very small, we expand  $\ln P(n)$  in a Taylor series about the value  $\langle n \rangle$ , as

$$\begin{aligned}\ln P(n) &= \ln P(\langle n \rangle) + \left[ \frac{d}{dn} \ln P(n) \right] (n - \langle n \rangle) \\ &\quad + \frac{1}{2!} \left[ \frac{d^2}{dn^2} \ln P(n) \right] (n - \langle n \rangle)^2 + \dots\end{aligned}$$

We may neglect higher powers, since  $n - \langle n \rangle$  is very small.

Now from Eq. (2.68) at  $n = \langle n \rangle$ ,  $\frac{d}{dn} \ln P(n) = 0$ .

$$\text{and } \frac{d^2}{dn^2} \ln P(n) = -\frac{N}{n(N-n)} = -\frac{N}{Np(N-Np)} = -\frac{1}{Npq}$$

$$\text{Hence, } \ln P(n) = \ln P(\langle n \rangle) - \frac{(n - \langle n \rangle)^2}{2Npq}$$

$$\text{or } P(n) = P(\langle n \rangle) e^{-\frac{(n - \langle n \rangle)^2}{2Npq}} \quad \dots(2.71)$$

The value of  $P(\langle n \rangle)$  can be found from the normalization condition

$$\sum P(n) = \sum P(\langle n \rangle) e^{-\frac{(n - \langle n \rangle)^2}{2Npq}} = 1$$

Putting  $x = n - \langle n \rangle$  and replacing summation by integration, we have

$$\sum P(n) = \int_{-\infty}^{\infty} P(\langle n \rangle) e^{-x^2/2Npq} dx$$

$$\text{Let } y = \frac{x}{\sqrt{2Npq}}$$

$$\begin{aligned}\text{Therefore, } \sum P(n) &= P(\langle n \rangle) \int_{-\infty}^{\infty} e^{-y^2} \sqrt{2Npq} dy \\ &= P(\langle n \rangle) \sqrt{2Npq} \cdot \sqrt{\pi} = 1 \text{ (see Appendix B)}$$

$$\text{Therefore, } P(\langle n \rangle) = \frac{1}{\sqrt{2\pi Npq}}$$

$$\text{and } P(n) = \frac{1}{\sqrt{2\pi Npq}} e^{-\frac{(n - \langle n \rangle)^2}{2Npq}} \quad \dots(2.72)$$

This expression is easier to evaluate, since it does not involve factorials of large numbers.

**Example 2.15.** With the data given in Ex. 2.13, calculate the probability distribution using Gaussian distribution formula. Depict the results obtained in the two causes graphically.

From Ex. 2.13 we have

$$N = 6, p = q = \frac{1}{2}$$

**Solution.** A glance at the table and Fig. 2.10 shows that even at such a small value of  $N$  and  $n$ , the results obtained are very close. For larger  $N$  the difference becomes still insignificant.

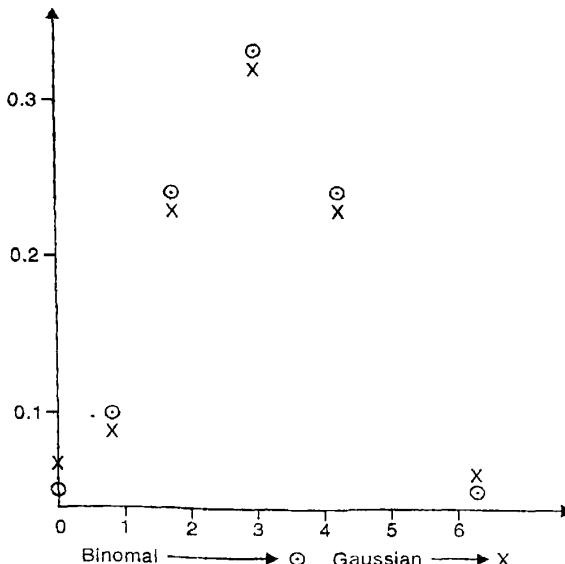


Fig. 2.10

X	Binomial		Gaussian	
	P(n)		P(n)	
0	0.0156		0.0162	
1	0.0937		0.0858	
2	0.2343		0.2333	
3	0.3125		0.3157	
4	0.2343		0.2333	
5	0.0937		0.0858	
6	0.0156		0.0162	

## 2.19 STANDARD DEVIATION IN THE CASE OF GAUSSIAN DISTRIBUTION

Standard deviation is given by

$$\begin{aligned}\sigma^2 &= \langle n^2 \rangle - \langle n \rangle^2 = \langle (n - \langle n \rangle)^2 \rangle \\ &= \sum (n - Np)^2 p(n)\end{aligned}$$

Putting  $x = n - Np$  and changing summation to integration, we have

$$\begin{aligned}\sigma^2 &= (2\pi Npq)^{-\frac{1}{2}} \int_{-\infty}^{\infty} e^{-x^2/2Npq} x^2 dx \\ &= Npq \quad (\text{see Appendix B})\end{aligned} \quad \dots(2.73)$$

and

$$\sigma = \sqrt{Npq} \quad \dots(2.74)$$

## 2.20 RANDOM WALK PROBLEM

The random walk problem is of considerable interest in statistical physics. We shall discuss this problem in this section as an application of the binomial distribution.

The original problem solved by Markoff can be formulated in the following way: A drunkard starts from a certain lamp post on a street. Some of the steps he takes are forward and some backward. Each step is of the same length and is completely independent of the preceding step. What is the probability that the drunkard, after taking  $N$  steps, will reach his destination, which is at a distance  $x$  from the lamp post?

A particle undergoing random displacements, as in Brownian motion, form a physical situation similar to a drunkard's tottering.

Consider a particle undergoing successive displacements each of length  $l$ , in one dimension. What is the probability that the particle, after  $N$  such displacements, will be at a distance  $x = ml$ , where  $m$  is an integer?

Let  $n_1$  be the number of displacements to the right and  $n_2$  to the left.

$$\text{Therefore, } N = n_1 + n_2 \quad \dots(2.75)$$

The net displacement, say, to the right is

$$ml = (n_1 - n_2) l = \{n_1 - (N - n_1)\} l = (2n_1 - N) l \quad \dots(2.76)$$

If the probability that the displacement is to the right is  $p$ , and that it is to the left is  $q = 1 - p$

then the probability of a sequence of  $n_1$  steps to the right

$$\text{and } n_2 \text{ steps to the left} = p^{n_1} q^{n_2} \quad \dots(2.77)$$

However, there are various ways in which a particle may undergo  $n_1$  displacements to the right and  $n_2$  to the left. For example, suppose a

particle undergoes 3 displacements, two of which are to the right and one to the left. This may happen in 3 different ways as shown (Fig. 2.11).

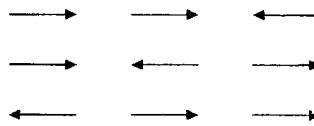


Fig. 2.11

The number of distinct possibilities in the problem we are considering is, therefore, equal to

$$\frac{N!}{n_1! n_2!} \quad \dots(2.78)$$

Therefore, the probability of  $n_1$  displacement to the right and  $n_2$  to the left in any order is

$$= \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2} \quad \dots(2.79)$$

Since the probability of a displacement in either direction is 1/2;  $p = q = \frac{1}{2}$ . Also from Eqs. (2.75) and (2.76)

$$n_1 = \frac{N+m}{2} \quad \text{and} \quad n_2 = \frac{N-m}{2} \quad \dots(2.80)$$

Therefore, the probability that the particle will be at  $x = ml$  after  $N$  displacements is given by

$$P_n(m) = C \cdot \frac{N!}{\left(\frac{N+m}{2}\right)! \left(\frac{N-m}{2}\right)!} \left(\frac{1}{2}\right)^N \quad \dots(2.81)$$

where  $C$  is the normalizing constant

Taking logarithms

$$\ln P_N(m) = \ln C + \ln N! - N \ln 2 - \ln \left(\frac{N+m}{2}\right)! - \ln \left(\frac{N-m}{2}\right)! \quad \dots(2.82)$$

Using Stirling's formula

$$\ln n! = n \ln n - n + \frac{1}{2} \ln (2\pi n) \quad \dots(2.83)$$

$$\begin{aligned} \ln P_N(m) &= \ln C + N \ln N - N + \frac{1}{2} \ln 2\pi + \frac{1}{2} \ln N \\ &\quad - N \ln 2 - \left\{ \frac{N}{2} \left( 1 + \frac{m}{N} \right) \right\} \ln \left\{ \frac{N}{2} \left( 1 + \frac{m}{N} \right) \right\} \end{aligned}$$

$$\begin{aligned}
 & + \frac{N}{2} \left( 1 + \frac{m}{n} \right) - \frac{1}{2} \ln 2\pi - \frac{1}{2} \ln \left\{ \frac{N}{2} \left( 1 + \frac{m}{N} \right) \right\} \\
 & - \left\{ \frac{N}{2} \left( 1 - \frac{m}{N} \right) \right\} \ln \left\{ \frac{N}{2} \left( 1 - \frac{m}{N} \right) \right\} + \frac{N}{2} \left( 1 - \frac{m}{N} \right) \\
 & - \frac{1}{2} \ln 2\pi - \frac{1}{2} \ln \left\{ \frac{N}{2} \left( 1 - \frac{m}{N} \right) \right\}
 \end{aligned} \quad \dots(2.84)$$

If  $m \ll N$ , which is generally true

$$\ln \left( 1 \pm \frac{m}{N} \right) = \pm \frac{m}{N} - \frac{m^2}{2N^2} \pm \dots$$

Substituting this in Eq. (2.84) and simplifying

$$\ln P_N(m) = \ln \left( \frac{4C^2}{2\pi N} \right)^{\frac{1}{2}} - \frac{m^2}{2N}$$

$$\text{Therefore } P_N(m) = C \left( \frac{2}{\pi N} \right)^{\frac{1}{2}} e^{-m^2/2N}$$

$$\text{Now } \int_{-\infty}^{\infty} P(m) dm = 1$$

$$\begin{aligned}
 \text{Therefore } & C \left( \frac{2}{\pi N} \right)^{\frac{1}{2}} \int_{-\infty}^{\infty} e^{-\frac{m^2}{2N}} dm \\
 & = C \left( \frac{2}{\pi N} \right)^{\frac{1}{2}} \cdot 2 \sqrt{2\pi N} \cdot \frac{\sqrt{\pi}}{2} \\
 & = 2C = 1
 \end{aligned}$$

or

$$C = \frac{1}{2}$$

$$\text{and } P_N(m) dm = \left( \frac{1}{2\pi N} \right)^{\frac{1}{2}} e^{-\frac{m^2}{2N}} \quad \dots(2.85)$$

This is the probability function for  $m$  excess displacements to the right. We can find the expression for the probability in terms of the distance  $x$  and time  $t$  by substituting in Eq. (2.85),  $x = ml$  and  $N = nt$ .

$$\text{Therefore, } P(x) dx = \left( \frac{1}{2\pi l^2 nt} \right)^{1/2} e^{-\frac{x^2}{2l^2 nt}} dx \quad \dots(2.86)$$

This is the normal or Gaussian distribution.

## PROBLEMS

- 2.1 A simple pendulum performs harmonic oscillations according to the law

$$\phi = \phi_0 \cos \frac{2\pi}{T} t$$

where  $\phi_0$  is the maximum angular deviation and  $T$  is the period. What is the probability that in a random measurement, the value of the angle of deviation lies between  $\phi$  and  $\phi + d\phi$ ?

- 2.2 Assume that the front and rear wheel axles of bicycles are manufactured in different workshops and that for every ten thousand front wheel axles one is defective; while for every ten thousand rear wheel axles two are defective. What is the probability for a bicycle picked at random to have two defective axles?
- 2.3 Workshop *A* manufactures high quality parts at the probability 0.8. Workshop *B* manufactures them at a probability 0.9. Three parts made by workshop *A* and four made by workshop *B* are taken at random. Find the probability for all seven parts to be good.
- 2.4 Five coins are tossed up simultaneously. Find the probability that at least one head turns up.
- 2.5 The probability for an archer hitting a target is 10%. If he shoots ten times independently what is the probability that the target will be hit at least once?
- 2.6 In a game, five dice are tossed simultaneously. Find the probability that an ace appears uppermost
- (a) in exactly one die
  - (b) in at least one die
  - (c) in exactly two dice
- 2.7 An urn contains 20 white and 10 black identical balls. Find the probability of successively drawing
- (i) two white balls; (ii) one white and one black ball, under the condition that after the first trial the ball is (a) returned (b) not returned to the urn.
- 2.8 The component  $\mu$  of the magnetic moment of a spin 1 particle can have 3 possible values:  $\mu_0$ , 0,  $-\mu_0$ . If the probability  $p$  that  $\mu = \mu_0$  is equal to the probability that  $\mu = -\mu_0$  calculate
- (i)  $\langle \mu \rangle$
  - (ii)  $\langle \mu^2 \rangle$
  - (iii)  $\langle (\Delta\mu)^2 \rangle$
- 2.9 A book of 600 pages contains 600 typographical errors. Assuming that these errors occur at random, use Poisson distribution to calculate the probability
- (a) that a page contains no errors
  - (b) that a page contains at least three errors.
- 2.10 A man who was carousing for the evening, decides to return home. However, his power of decision becomes completely random. He is 100 steps from his door. What is the probability that he arrives home in 100 steps?



It would be interesting to see how Maxwell introduced the probability concept in the kinetic theory of gases and derived the correct formula for the velocity distribution in the molecules of an ideal gas. This was quite an amazing achievement and marks the beginning of a new epoch in physics.

### 3.1 MAXWELL VELOCITY DISTRIBUTION

If  $f(u_x)$ ,  $f(u_y)$ ,  $f(u_z)$  are the distribution functions of the molecules in the three mutually perpendicular directions, the probabilities that the molecules have velocity components between  $u_x$  and  $u_x + du_x$ ,  $u_y$  and  $u_y + du_y$ ,  $u_z$  and  $u_z + du_z$  are  $f(u_x)du_x$ ,  $f(u_y)du_y$ ,  $f(u_z)du_z$ , respectively. Maxwell's derivation was based on the following two assumptions :

- (i) The distribution of molecules moving from a point in any direction is isotropic; otherwise, the molecules would drift in a preferred direction. All directions in space are equivalent and, hence, any direction of velocity of a molecule is equally probable.

Therefore  $f(u_x)du_x = f(u_y)du_y = f(u_z)du_z$  ... (3.1)  
where  $f$  is always the same function.

- (ii) The movements of the molecules along the three mutually perpendicular directions are independent. That is  $u_x$ ,  $u_y$ ,  $u_z$  are independent of each other.

Note, however, that this second assumption holds only for velocities smaller than the velocity of light. If the molecules move with the velocity of light  $c$ , the velocity components are no longer independent, since they are related to  $c$  by the equation.

$$u_x^2 + u_y^2 + u_z^2 = c^2 \quad \dots (3.2)$$

The formula we derive here is, therefore, valid only in non-relativistic mechanics.

From Maxwell's second assumption the number of molecules with velocities in the range  $u_x$  and  $u_x + du_x$ ,  $u_y$  and  $u_y + du_y$ ,  $u_z$  and  $u_z + du_z$

$$N = N_0 f(u_x) f(u_y) f(u_z) du_x du_y du_z \quad \dots (3.3)$$

where  $N_0$  is the total number of molecules of the gas.

In this equation  $du_x du_y du_z$  can be considered as volume element in the velocity space and  $f(u_x) f(u_y) f(u_z)$  as the probability density of velocity.

Because of the property of isotropy, the probability for the components  $u_x$  and  $-u_x$  should be the same. Hence, the probability density function  $f(u_x)$  must be an even function of  $u_x$ . We therefore, write

$$f(u_x) = \phi(u_x^2); f(u_y) = \phi(u_y^2); f(u_z) = \phi(u_z^2) \quad \dots(3.4)$$

where  $\phi$  is the same function in all three cases.

Now if  $u$  is the resultant velocity, the probability density of velocity is

$$\psi(u^2) = f(u_x) f(u_y) f(u_z) = \phi(u_x^2) \phi(u_y^2) \phi(u_z^2) \quad \dots(3.5)$$

We have now to determine the form of the functions  $\psi$  and  $\phi$ .

Taking logarithms

$$\ln\psi(u^2) = \ln\phi(u_x^2) + \ln\phi(u_y^2) + \ln\phi(u_z^2) \quad \dots(3.6)$$

Differentiating with respect to  $u_x$ , we have

$$\frac{1}{\psi(u^2)} \frac{\partial\psi(u^2)}{\partial(u^2)} 2u_x = \frac{1}{\phi(u_x^2)} \frac{\partial\phi(u_x^2)}{\partial(u_x^2)} \cdot 2u_x$$

$$\text{i.e.} \quad \frac{1}{\phi(u_x^2)} \frac{\partial\phi(u_x^2)}{\partial(u_x^2)} = \frac{1}{\psi(u^2)} \frac{\partial\psi(u^2)}{\partial(u^2)} \quad \dots(3.7)$$

Similarly,

$$\frac{1}{\phi(u_y^2)} \frac{\partial\phi(u_y^2)}{\partial(u_y^2)} = \frac{1}{\psi(u^2)} \frac{\partial\psi(u^2)}{\partial(u^2)} \quad \dots(3.8)$$

and

$$\frac{1}{\phi(u_z^2)} \frac{\partial\phi(u_z^2)}{\partial(u_z^2)} = \frac{1}{\psi(u^2)} \frac{\partial\psi(u^2)}{\partial(u^2)} \quad \dots(3.9)$$

Hence,

$$\frac{1}{\phi(u_x^2)} \frac{\partial\phi(u_x^2)}{\partial(u_x^2)} = \frac{1}{\phi(u_y^2)} \frac{\partial\phi(u_y^2)}{\partial(u_y^2)} = \frac{1}{\phi(u_z^2)} \frac{\partial\phi(u_z^2)}{\partial(u_z^2)} = -\alpha \quad \dots(3.10)$$

where  $\alpha$  is a constant. The negative sign has been introduced for convenience.

Integrating the equation

$$\frac{1}{\phi(u_x^2)} \frac{\partial\phi(u_x^2)}{\partial(u_x^2)} = -\alpha$$

We have

$$\phi(u_x^2) = Ce^{-\alpha u_x^2} \quad \dots(3.11)$$

where  $C$  is another constant.

The probability that the molecule has components between  $u_x$  and  $u_x + du_x$  is

$$f(u_x)du_x = Ce^{-\alpha u_x^2} du_x \quad \dots(3.12)$$

The constant  $C$  can be found from the normalization condition

$$\int_{-\infty}^{\infty} f(u_x)du_x = \int_{-\infty}^{\infty} Ce^{-\alpha u_x^2} du_x = 1 \quad \dots(3.13)$$

Since the integral must converge,  $\alpha$  must necessarily be positive. Now

$$\int_{-\infty}^{\infty} Ce^{-\alpha u_x^2} du_x = C \sqrt{\frac{\pi}{\alpha}} = 1 \quad (\text{See Appendix B})$$

$$\text{Therefore, } C = \sqrt{\frac{\alpha}{\pi}} \text{ and } f(u_x) du_x = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha u_x^2} du_x \quad \dots(3.14)$$

Hence, the number of molecules whose velocity lies between  $u$  and  $u + du$  is

$$N(u) du = N_0 \left( \frac{\alpha}{\pi} \right)^{3/2} e^{-\alpha u^2} du_x du_y du_z \quad \dots(3.15)$$

or using spherical polar coordinates

$$N(u) du = 4\pi N_0 \left( \frac{\alpha}{\pi} \right)^{3/2} e^{-\alpha u^2} u^2 du \quad \dots(3.16)$$

We have now to identify the parameter  $\alpha$ .

We first calculate the pressure of a gas contained in a vessel of volume  $V$ . In the equilibrium state, the molecule will be distributed over the volume of the vessel in a uniform manner in such a way that their concentrations is  $n = N/V$ , independently of the coordinates at the point where the measurement are made. The number density of the molecules with velocities between  $u_x$  and  $u_x + du_x$  is

$$n(u_x) = n \left( \frac{\alpha}{\pi} \right)^{1/2} e^{-\alpha u_x^2} du_x \quad \dots(3.17)$$

The number of molecules hitting a unit area of the wall perpendicular to  $u_x$  per unit time, is equal to the number in the parallelepiped of volume  $u_x$

$$= n \left( \frac{\alpha}{\pi} \right)^{1/2} e^{-\alpha u_x^2} u_x du_x \quad \dots(3.18)$$

Every time a molecule hits the wall, there is a change in momentum equal to  $mu_x - (-mu_x) = 2mu_x$ . In other words the momentum transferred to the wall is  $2mu_x$ . Hence, the momentum transferred per unit area of the wall per unit time.

$$= n \left( \frac{\alpha}{\pi} \right)^{1/2} e^{-\alpha u_x^2} 2m u_x du_x \quad \dots(3.19)$$

The total momentum transferred is equal to the force which in the present case is the pressure  $P$

$$\begin{aligned} P &= \int_0^\infty n \left( \frac{\alpha}{\pi} \right)^{1/2} e^{-\alpha u_x^2} 2m u_x^2 du_x \\ &= n \left( \frac{\alpha}{\pi} \right)^{1/2} 2m \int_0^\infty u_x^2 e^{-\alpha u_x^2} du_x \\ &= n \left( \frac{\alpha}{\pi} \right)^{1/2} 2m \frac{\sqrt{\pi}}{4\alpha^{3/2}} = \frac{nm}{2\alpha} \end{aligned} \quad \dots(3.20)$$

The equation of state of a gas is

$$P = nkT \quad \dots(3.21)$$

where  $K$  is Boltzmann constant and  $K = 1.38 \times 10^{-23}$  Joule/K.

Comparing Eqs. (3.20) and (3.21), we have

$$nkT = \frac{nm}{2\alpha}, \text{ i.e. } \alpha = \frac{m}{2kT} \quad \dots(3.22)$$

Using this value in Eq. (3.16) we have

$$N(u)du = 4\pi N_0 \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mu^2/2kT} u^2 du \quad \dots(3.23)$$

### 3.2 MOMENTUM DISTRIBUTION

Using the relation  $p = mu$ , we can transform Eq. (3.23) in terms of momentum,

i.e.

$$N(p) dp = 4\pi N_0 \left( \frac{1}{2\pi m k T} \right)^{3/2} e^{-p^2/2mkT} p^2 dp \quad \dots(3.24)$$

### 3.3 ENERGY DISTRIBUTION

The energy distribution can be found in the same way using

$$\varepsilon = \frac{1}{2} mu^2; \quad d\varepsilon = mudu = \sqrt{2\varepsilon} m du \quad \dots(3.25)$$

Substituting these values in Eq. (3.23), we have

$$N(\varepsilon) d\varepsilon = 4\pi N \left( \frac{m}{2\pi k T} \right)^{3/2} e^{-\varepsilon/kT} \frac{2\varepsilon}{m} \frac{d\varepsilon}{\sqrt{2\varepsilon m}} \quad \dots$$

$$= \frac{2N}{\sqrt{\pi}} \left( \frac{1}{kT} \right)^{3/2} e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon \quad \dots(3.26)$$

### 3.4 SOME SIGNIFICANT MEAN VALUES

(i) Mean value of  $u^n$

$$\langle u^n \rangle = \int u^n f(u) du = \int 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mu^2/2kT} u^{n+2} du$$

where we have used Eq. (3.23)

$$\begin{aligned} &= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^\infty e^{-mu^2/2kT} u^{n+2} du \\ &= 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{1}{2 \left( \frac{m}{2kT} \right)^{n+3}} \Gamma \left( \frac{n+3}{2} \right) \text{(See Appendix B)} \\ &= \frac{2}{\sqrt{\pi}} \left( \frac{2kT}{m} \right)^{n/2} \Gamma \left( \frac{n+3}{2} \right) \end{aligned} \quad \dots(3.27)$$

The mean speed  $\langle u \rangle$  is

$$\langle u \rangle = \frac{2}{\pi} \left( \frac{2kT}{m} \right)^{n/2} \Gamma(2) = \sqrt{\frac{8kT}{\pi m}} \quad \dots(3.28)$$

(ii) Root mean square speed

$$\langle u^2 \rangle = \frac{2}{\sqrt{\pi}} \left( \frac{2kT}{m} \right)^{1/2} \Gamma \left( \frac{5}{2} \right) = \frac{3kT}{\pi m}$$

$$\text{Therefore, } \sqrt{\langle u^2 \rangle} = \sqrt{\frac{3kT}{m}} \quad \dots(3.29)$$

(iii) The most probable speed  $\tilde{u}_p$ .

The most probable speed  $\tilde{u}_p$  of a molecule is the speed for which the probability  $P(u)$  is maximum. The condition for  $P(u)$  to be maximum is

$$\frac{\partial P(u)}{\partial u} = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \left[ 2u - \frac{mu^3}{kT} \right] e^{-mu^2/2kT} = 0$$

$$\text{Therefore, } \tilde{u}_p = \sqrt{\frac{2kT}{m}}$$

$\dots(3.30)$

Figure 3.1 shows the relative values of the three speeds.

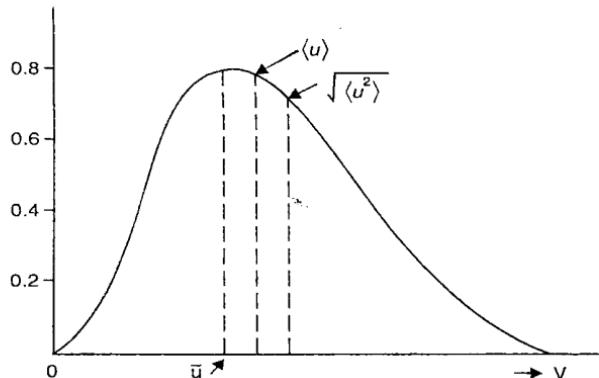


Fig. 3.1

(iv) Mean energy

$$\langle \epsilon \rangle = \int_0^{\infty} \epsilon \frac{2N}{\sqrt{\pi}} \frac{1}{(kT)^{3/2}} e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon$$

where we have used Eq. (3.26)

$$\langle \epsilon \rangle = \frac{2N}{\sqrt{\pi}} \cdot \frac{1}{(kT)^{3/2}} \int_0^{\infty} \epsilon^{3/2} e^{-\epsilon/kT} d\epsilon$$

Putting  $x = \sqrt{\epsilon}$ ,  $dx = \frac{1}{2\sqrt{\epsilon}} d\epsilon$

$$\begin{aligned} \text{Therefore } \langle \epsilon \rangle &= \frac{2N}{\sqrt{\pi}} \cdot \frac{1}{(kT)^{3/2}} \int_0^{\infty} 2x^4 e^{-x^2/kT} dx \\ &= \frac{4N}{\sqrt{\pi}} \cdot \frac{1}{(kT)^{3/2}} \cdot \frac{1}{2\left(\frac{1}{kT}\right)^{5/2}} \Gamma\left(\frac{5}{2}\right) \end{aligned}$$

$$= \frac{3}{2} N k T \quad \dots(3.31)$$

This shows that, on an average, energy  $\frac{1}{2} kT$  is associated with each molecule for each degree of freedom.

### 3.5 EXPERIMENTAL VERIFICATION OF MAXWELL DISTRIBUTION

We describe in this section a few experiments out of the many that were carried out to verify experimentally Maxwell distribution.

#### 3.5.1 Stern's Experiment

A cross-section of the experimental arrangement used by Stern for the verification of Maxwell distribution is shown in Fig. 3.2.

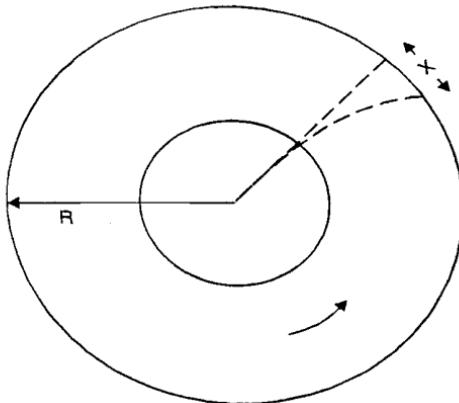


Fig. 3.2

A platinum filament coated with a layer of silver is placed along the axis of two rotating co-axial cylinders. The filament is heated to such a temperature that silver begins to evaporate. A slot is made on the inner cylinder so that some of the evaporated atoms fly through the slot towards the outer cylinder where they are deposited. If the two cylinders were stationary, the atoms deposited on the outer cylinder would form the image of the slot directly opposite to the slot. The cylinders, however, are rotating with a certain angular velocity  $\omega$ . Hence, during the time the atoms fly from the slot to the outer cylinder, the latter has moved through a distance  $x$  and the atoms will be deposited at a point which is not directly opposite to the slot.

If  $u$  is the velocity of the atoms and  $d$  the separation between cylinders, the duration of the flight is given by

$$\Delta t = \frac{d}{u} \quad \dots(3.32)$$

During this time, the outer cylinder has turned through an angle  $\Delta\psi$  given by

$$\Delta\psi = \omega \Delta t \quad \dots(3.33)$$

The coordinate  $x$  measured from the point opposite the slot is

$$x = R \Delta \psi = R \omega \Delta t = R \omega \frac{d}{u} \quad \dots(3.34)$$

For the gas to obey Maxwell distribution there must not be any interaction of the molecules with one another, hence, a high vacuum will have to be created in the vessel. In order that the molecules emerging from the slot have the same distribution as in the inner cylinder, we have to ensure that the gas flows through the slot without any hydrodynamic pressure. Such a collision-free emergence of atoms is possible if the size of the slot is very small, smaller than the mean free path of the atoms.

If we assume that the evaporated atoms obey Maxwell distribution, the flux of atoms passing through the slot an having their velocities between  $u$  and  $u + du$  is

$$\begin{aligned} |J| &= C \left( \frac{m}{2\pi kT} \right)^{3/2} u^2 e^{-mu^2/2kT} du \\ &= C \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{(Rod)^3}{x^4} e^{-\frac{m}{2kT} \left( \frac{Rod}{x} \right)^2} dx \quad \dots(3.35) \end{aligned}$$

where  $C$  is a constant depending on the parameters of the arrangement. This formula determines the distribution of the atoms deposited on the outer cylinder. The thickness of the layer deposited can be taken as a measure of the number of molecules. The measurement of the thickness against  $x$  agreed with Eq. (3.35), thus confirming Maxwell distribution.

### 3.5.2 Free Fall under Gravity

Twenty-five years later, a more elegant experiment was suggested again by Stern and his colleagues, in which the force of gravity was the selector. The atoms or molecules which effuse from the horizontal slit in the oven, are registered by a detector  $D$  (Fig. 3.3). In gravitational field, slower

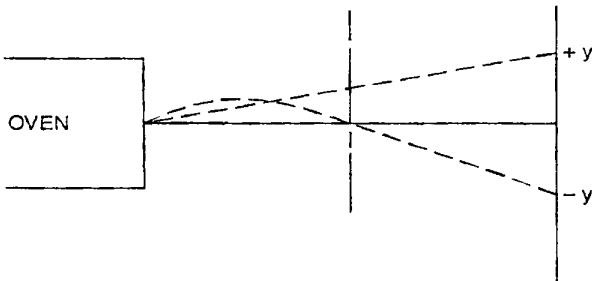


Fig. 3.3

molecules deviate towards the Earth to a larger extent than faster molecules. The deviation can be easily calculated as a function of velocity. The velocity of a molecule is analyzed in the same way as the trajectory of a bullet. A molecule leaving the oven towards  $+y$  and passing through the middle slit, strikes the detector at  $-y$ . The number of molecules arriving at  $-y$  are directly proportional to the flow distribution. Although the deviations observed in such experiments are of the order of several tenths of a millimeter, the experiments can be carried out reliably and confirm the validity of Maxwell distribution.

### 3.5.3 The Doppler Broadening of Spectral Lines

An experimental verification of the Maxwell distribution function is obtained by measuring the width of a spectral line emitted by the hot gas molecules at low densities. This broadening is due to what is known as Doppler effect, which arises from the distribution of velocities of the molecules in the gas.

Suppose a molecule moving with a velocity  $v_z$  towards an observer is emitting a radiation of wavelength  $\lambda_0$  in the direction of motion. The wavelength  $\lambda$  as recorded by the observer, will be different from  $\lambda_0$  and will be related to it by the Doppler expression

$$\lambda = \lambda_0 \left(1 - \frac{v_z}{c}\right) \quad \dots(3.36)$$

$$\therefore v_z = \frac{c(\lambda_0 - \lambda)}{\lambda_0} \quad \dots(3.37)$$

and  $dv_z = -c \frac{d\lambda}{\lambda_0}$  ...(3.38)

The negative sign relates to the direction for  $v_z$ .

The probability that a molecule has a component velocity in the range from  $v_z$  to  $v_z + dv_z$ , is

$$\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_z^2/2kT} dv_z$$

i.e.  $\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mc^2(\lambda_0 - \lambda)^2}{2kT(\lambda_0)}} \frac{C}{\lambda_0} d\lambda$

Therefore, the intensity of radiation  $I_\lambda d\lambda$  received by the observer will be proportional to

$$\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{mc^2(\lambda_0 - \lambda)^2}{2kT(\lambda_0)}} \frac{C}{\lambda_0} d\lambda$$

i.e.  $I_\lambda d\lambda = C^1 e^{-\frac{mc^2(\lambda_0 - \lambda)^2}{2kT(\lambda_0)}} d\lambda \quad \dots(3.39)$

where  $C^1 = \left(\frac{m}{2\pi kT}\right)^{1/2} \frac{C}{\lambda_0}$

When  $\lambda = \lambda_0, I_{\lambda_0} = C^1$

$$I_\lambda d\lambda = I_{\lambda_0} e^{-\frac{mc^2(\lambda_0 - \lambda)^2}{2kT(\lambda_0)}} d\lambda \quad \dots(3.40)$$

The distribution of intensity, thus, has a Gaussian line shape (Fig. 3.4).

The width of a spectral line is usually measured at the half-intensity points (Fig. 3.4). If Eq. (3.40) is expressed in terms of frequency one can easily find that the half intensity width  $\Delta\nu_d$  is given on the frequency scale by

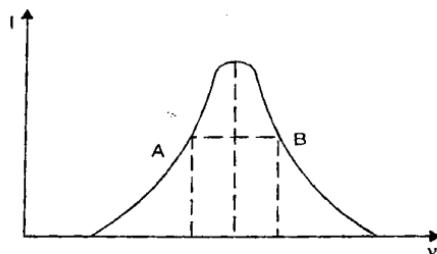


Fig. 3.4

$$\frac{\Delta\nu_d}{\nu_0} = \left( \frac{\nu_{+1/2} - \nu_{-1/2}}{\nu_0} \right) = 2 \left( \frac{2kT \ln 2}{mc^2} \right)^{3/2} \quad \dots(3.41)$$

The agreement between theory and experiment has been found to be excellent.

### 3.6 FRACTION OF MOLECULES IN A GAS WITH ENERGIES HIGHER THAN A CERTAIN VALUE $\varepsilon_0$

It is known that when the velocity of molecules exceeds a certain value  $u_0$ , the collisions between molecules becomes violent and result in bimolecular reactions. For example, a reaction of the thermonuclear fusion, in which two deuterium nuclei combine to form a helium nucleus can proceed only if deuterium nuclei have sufficiently large energy. In the same way, for a gas discharge plasma to exist the electrons in it must have an energy sufficient for ionization of neutral atoms. In the study of such cases, it becomes imperative to calculate the fraction of particle having velocities in excess of a certain value  $u_0$ .

#### (i) One-dimensional problem

We first consider the problem in one dimension. From Eq. (3.41), the fraction of molecules having velocities exceeding  $u_x$  is

$$f_1 = 2 \left( \frac{m}{2\pi kT} \right)^{1/2} \int_{u_0}^{\infty} e^{-mu_x^2/2kT} du_x \quad \dots(3.42)$$

We have introduced in this equation a factor 2 in order to take account of the molecules moving in both directions.

Putting  $x^2 = \frac{mu_x^2}{2kT}$ ,  $du_x = \sqrt{\frac{2kT}{m}} dx$

$$f_1 = \frac{2}{\sqrt{\pi}} \int_{x_0}^{\infty} e^{-x^2} dx \quad \dots(3.43)$$

where

$$x_0 = \sqrt{\frac{m}{2kT}} u_0$$

This integral cannot be evaluated explicitly but we can obtain its value to a good approximation as shown in Appendix B.

Thus

$$f_1 = \left( \frac{1}{\pi x_0} \right)^{1/2} e^{-x_0^2} = \left( \frac{2kT}{\pi m u_x^2} \right)^{1/2} e^{-mu_x^2/kT} \quad \dots(3.44)$$

or in terms of kinetic energy

$$f_1 = \left( \frac{kT}{\pi \epsilon_0} \right)^{1/2} e^{-\epsilon_0/kT} \quad \dots(3.45)$$

**Example 3.1** Find the fraction of H<sub>2</sub> and N<sub>2</sub> molecules at the surface of (i) the earth; (ii) the moon, having velocities (away from the centre) higher than their escape velocities. Assume the temperature to be 300K. What information do these calculations give about the atmosphere of the earth and the moon?

	Earth	Moon
Mass	$5.976 \times 10^{24} \text{ kg}$	$7.400 \times 10^{22} \text{ kg}$
Radius	$6.378 \times 10^6 \text{ m}$	$1.740 \times 10^6 \text{ m}$

$$\text{Escape velocity} = \sqrt{\frac{2GM}{R}}$$

$$\text{Earth} \quad u_{x_0} = \frac{\sqrt{2 \times 6.67 \times 10^{-11} \times 5.976 \times 10^{24}}}{6.378 \times 10^6} = 1.12 \times 10^4 \text{ m/s}$$

$$\text{Moon} \quad u_{x_0} = \frac{\sqrt{2 \times 6.67 \times 10^{-11} \times 7.400 \times 10^{22}}}{1.440 \times 10^6} = 2.38 \times 10^3 \text{ m/s}$$

$$\text{Now} \quad f_1 = \frac{1}{2} \left( \frac{2kT}{\pi m u_x^2} \right)^{1/2} e^{-mu_x^2/2kT}$$

(The factor 1/2 has been introduced, because the other half moves in the opposite direction).

Substituting actual values in the above expression we have

$$H_2 \quad N_2$$

$$f_1 = \begin{cases} \text{Earth} & \sim 10^{-23} \quad 2 \times 10^{-2} \\ \text{Moon} & \sim 10^{-307} \quad 10^{-15} \end{cases}$$

We see that the rate of escape of the molecules from the surface of the moon is much faster compared to that from the surface of the earth. This explains the absence of lunar atmosphere.

(ii) **Two-dimensional problem.** Velocity distribution function in this case is

$$\begin{aligned} & \left( \frac{m}{2\pi kT} \right) e^{-m(u_x^2 + u_y^2)/2kT} du_x du_y \\ & = 2\pi u \cdot \frac{m}{2\pi kT} e^{-mu^2/2kT} \cdot du = \frac{mu}{kT} e^{-mu^2/2kT} du \end{aligned} \quad \dots(3.46)$$

where we have put  $u^2 = u_x^2 + u_y^2$  and  $2\pi u du = du_x du_y$ . Hence the fraction of molecules having velocities higher than  $u_0$  is

$$\begin{aligned} f_2 &= \int_{u_0}^{\infty} \frac{mu}{kT} e^{-mu^2/2kT} du \\ &= \int_{x_0}^{\infty} e^{-x} dx \left\{ \text{putting } x = \frac{mu^2}{2kT} \right\} \\ &= e^{-x_0} = e^{-mu_0^2/2kT} = e^{-e_0/kT} \end{aligned} \quad \dots(3.47)$$

(iii) **Three-dimensional problem.** The fraction of molecules having velocities exceeding a certain value  $u_0$  is

$$f_3 = \int_{u_0}^{\infty} 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-mu^2/2kT} u^2 du \quad \dots(3.48)$$

Let  $x^2 = \frac{mu^2}{2kT}$

Therefore  $du = \sqrt{\frac{2kT}{m}} dx$

Hence

$$f_3 = \frac{4}{\sqrt{\pi}} \int_{x_0}^{\infty} x^2 e^{-x^2} dx = -\frac{2}{\sqrt{\pi}} \int_{x_0}^{\infty} x d(e^{-x^2})$$

Integrating by parts

$$\begin{aligned} f_3 &= \left[ -\frac{2}{\sqrt{\pi}} x e^{-x^2} \right]_{x_0}^{\infty} + \frac{2}{\sqrt{\pi}} \int_{x_0}^{\infty} e^{-x^2} dx \\ &= \frac{2}{\sqrt{\pi}} x_0 e^{-x_0^2} + \frac{2}{\sqrt{\pi}} \left[ \int_0^{\infty} e^{-x^2} dx - \int_0^{x_0} e^{-x^2} dx \right] \\ &= \frac{2}{\sqrt{\pi}} x_0 e^{-x_0^2} + 1 - \frac{2}{\sqrt{\pi}} \int_0^{x_0} e^{-x^2} dx. \end{aligned} \quad \dots(3.49)$$

The function

$$\frac{2}{\pi} \int_0^{x_0} e^{-x^2} dx = \operatorname{erf} x_0 \quad \dots(3.50)$$

is known as the *error function*. This occurs frequently in calculations. It is evaluated numerically and its values for various  $x_0$  are tabulated in mathematical literature. The values of the error function when  $x_0 \ll 1$  and  $x_0 \gg 1$ , can be found without the aid of tables as has been shown in Appendix B.

For

$$x_0 \ll 1 \quad \left\{ \begin{array}{l} \text{erf } x_0 = \frac{2}{\sqrt{\pi}} \left( x_0 - \frac{x_0^2}{3} \right) \end{array} \right. \quad \dots(3.51)$$

$$x_0 \gg 1 \quad \left\{ \begin{array}{l} \text{erf } x_0 = 1 - \frac{1}{\sqrt{\pi} x_0} \left( 1 - \frac{1}{2x_0^2} \right) e^{-x_0^2} \end{array} \right. \quad \dots(3.52)$$

Hence, for  $x_0 \ll 1$

$$f_3 = \frac{2}{\sqrt{\pi}} x_0 e^{-x_0^2} = \frac{1}{\sqrt{\pi} x_0} \left( 1 - \frac{1}{2x_0^2} \right) e^{-x_0^2}$$

If  $x_0$  is very much greater than unity,

$$f_3 = \frac{2}{\sqrt{\pi}} x_0 e^{-x_0^2} = \frac{2}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{1/2} u_0 e^{-mu_0^2/2kT} \quad \dots(3.53)$$

Or in terms of energy

$$f_3 = \frac{2}{\sqrt{\pi}} \left( \frac{\epsilon_0}{kT} \right) e^{-\epsilon_0/kT} \quad \dots(3.54)$$

**Example 3.2** The electron temperature of a gas discharge plasma in hydrogen is  $T = 20000\text{K}$ . Assuming that the distribution function of electrons is Maxwellian, find the fraction of electron that is capable of ionizing neutral hydrogen atoms. (Ionization energy of hydrogen is 13.5 eV.)

For ionization of neutral atoms, electrons must have energies higher than the ionization energy of the atoms, i.e. 13.5 eV.

Now 
$$f_3 = \frac{2}{\sqrt{\pi}} \sqrt{\frac{\epsilon_0}{kT}} e^{-\epsilon_0/kT}$$

$$\frac{\epsilon_0}{kT} = \frac{13.5 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 2 \times 10^4} = 7.8$$

(because 1 eV =  $1.6 \times 10^{-19}$  J)

$$\text{Therefore, } f_3 \approx \frac{2}{\sqrt{3.14}} \times 2.8 \times e^{-7.8} = 0.0013$$

That is, 0.13% of electrons are capable of ionizing neutral hydrogen atoms.

**PROBLEMS**

- 3.1 A vessel contains 0.1 kg of oxygen ( $O_2$ ). Find the number of oxygen molecules having their velocities between 200 and 210 m/s, the gas being maintained at 0°C.
- 3.2 Find the root mean square velocity of hydrogen ( $H_2$ ) gas at room temperature.
- 3.3 Show that for a Maxwellian gas, the fluctuation of the velocity is given by
- $$\langle (\Delta u)^2 \rangle = \frac{kT}{M} \left( 3 - \frac{3}{\pi} \right)$$
- 3.4 Find the temperature at which the root mean square speed of hydrogen gas molecules is just equal to the velocity of escape of the molecules from the earth.



## MACROSCOPIC AND MICROSCOPIC STATES

The treatment given in the preceding chapter was limited to the problems connected with the properties of ideal gases. We now proceed to describe a more general method for dealing with the problems in statistical physics. The method can be applied to a system much more complicated than a gas system, and of macroscopic dimensions, whose constituent particles may interact with one another.

A system is generally characterized by the physical and chemical properties of the substance in the space occupied by it, as well as by the properties of boundaries. In general, we are concerned with systems consisting of a large number of particles, such as for example, a gas comprising a large number of molecules contained in a vessel; or a crystal consisting of a large number of atoms in a lattice etc. The properties of a system depend upon the state in which it exists at the instant at which measurements are made. Our first concern, therefore will be how to specify the state of a system at any time.

### 4.1 MACROSCOPIC STATES

Logically since all system obey quantum mechanics we should start with quantum statistical physics and then arrive at classical statistical physics as a particular case. But it is not always necessary to use quantum mechanics in describing the behaviour of a thermodynamic system. Newtonian mechanics is in excellent approximation and, hence it, convenient to commence the study of statistical mechanics consideration.

To explain the concept of the state of a system, we will once more refer to a monatomic ideal gas, which is relatively a simple system. By an ideal gas we mean that its constituent particles have a finite mass, undergo elastic collisions with one another and with the boundary walls and have no other interaction of any kind. We further assume that the vessel containing the gas is isolated. That is, it does not exchange energy with the material bodies outside and, hence, all variations in the gas are due to internal reasons. The time spent in collision is very much shorter than the time lapse between collisions. It must be mentioned here that real gases are not ideal in the sense we have described above. They approximate to the ideal gases when the pressure is very low. Under this

condition the particle density is so low that the particles are relatively distant from each other. If a gas is left to itself for a sufficiently long time, the pressure and the temperature of the gas, whatever their initial distribution, stabilize over the entire volume and we say that the gas has attained a steady state. In this state the pressure ( $P$ ), temperature ( $T$ ) and volume ( $V$ ) remain constant in time. This state of the gas, characterized by the parameters,  $P$ ,  $T$  and  $V$ , is called its *macroscopic state*. The macroscopic steady state in this particular case is also called its equilibrium state. Note that a steady state is not always an equilibrium state. For a system that is not isolated, it is possible to establish a steady state by maintaining the different parts of the walls of the vessel at different temperatures with the help of external sources. We will however, restrict ourselves in the first few chapters to the study of equilibrium state, as these provide a great simplification. Besides most systems we encounter are in thermodynamics equilibrium or else they tend to reach very rapidly to a state of equilibrium.

## 4.2 MICROSCOPIC STATES

Since a gas consists of a large number of particles, the state of a gas can also be characterized in terms of the states of the constituent particles. The states of the particles can be specified by ascertaining their positions (coordinates  $q_i$ ) and velocities or momenta  $p_i$ . The state of the gas thus described in terms of the properties of its constituent particles is called its *macroscopic state*.

We have seen above that the quantities pressure, temperature and volume which describe the macroscopic state remain constant in the steady state of the gas. The constituent particles of the gas, however, are continuously in motion and undergo collisions even in a steady state and hence microscopic state keep on changing continuously. Let us be more clear on this point. The microscopic state of a gas at any instant is defined by the instantaneous positions and momenta (in magnitude and direction) of the various molecules. If any change is made in the molecular distribution, a new microscopic state results. Many of the different microscopic states, however, will be indistinguishable from the standpoint of macroscopic observation. For instance, if the positions and momenta of two or more molecules are interchanged, a new microscopic state will result; yet from the macroscopic point of view, no change will be detected in the condition of the gas. Each one of the microscopic states is said to pertain to the same macroscopic state. We are thus led to associate with each microscopic state a large number of microscopic states, although they widely differ in respect of their dynamical states.

Consider, for example, an ideal gas system in which particles can exist in any one of the states with energy equal to 0, 1, 2, 3 energy units and no other. Suppose the system of three distinguishable particles  $a$ ,  $b$  and  $c$  and the total energy of the system is three energy units. In how many ways three energy units can be distributed among the three

distinguishable particles, consistent with the condition that the total energy of the system is three units? In other words, how many microscopic states correspond to the macroscopic state specified by three energy units?

Figure 4.1 shows the possible configurations of the system and the number of microscopic states.

Configuration			Number of states																			
			Distinguishable particles	Indistinguishable particles																		
3 2 1 0	<table border="1"> <tr><td>a</td><td>b</td><td>c</td></tr> <tr><td></td><td></td><td></td></tr> <tr><td>bc</td><td>ac</td><td>2b</td></tr> </table>	a	b	c				bc	ac	2b		3	1									
a	b	c																				
bc	ac	2b																				
3 2 1 0	<table border="1"> <tr><td>a</td><td>a</td><td>b</td><td>b</td><td>c</td><td>c</td></tr> <tr><td>b</td><td>c</td><td>c</td><td>a</td><td>a</td><td>b</td></tr> <tr><td>c</td><td>b</td><td>a</td><td>c</td><td>b</td><td>b</td></tr> </table>	a	a	b	b	c	c	b	c	c	a	a	b	c	b	a	c	b	b		6	1
a	a	b	b	c	c																	
b	c	c	a	a	b																	
c	b	a	c	b	b																	
3 2 1 0	<table border="1"> <tr><td></td><td></td><td></td><td></td><td></td><td></td></tr> <tr><td></td><td></td><td></td><td></td><td></td><td></td></tr> <tr><td>abc</td><td></td><td></td><td></td><td></td><td></td></tr> </table>													abc						Total number of states	1	1
abc																						
			10	3																		

Fig. 4.1

The total number of accessible microscopic states corresponding to the single macroscopic states in ten of the particles are distinguishable and three if they are indistinguishable.

One of the aims of statistical mechanics is to correlate the properties of matter in bulk with the properties of its constituent particles i.e. to establish a relation between a macroscopic state and the corresponding microscopic states.

### 4.3 PHASE SPACE

We shall now show how the state of a system is specified. We assume that the physical systems obey the most general laws of dynamics as set down by Hamilton. The state of a system is determined when we know the details of its motion and, hence, is fully specified at a particular time by a certain number of generalized coordinates  $q_i$  and an equal number of generalized momenta  $p_i$ . These coordinates and momenta are governed by the canonical equation of Hamilton:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (i = 1, 2, \dots) \quad \dots(4.1)$$

where  $q_i$  are the generalized coordinates

$p_i$  are the generalized momenta

and  $H$  is Hamiltonian of the system

A most elementary physical realization of such a system is furnished by a single particle constrained to move in a straight line. The position of the particle at any time can be described by giving its distance from a fixed point on the line—origin of coordinates. This single numerical fact merely gives its ‘mechanical configuration’ at the time in question. For the complete specification of its state, its momentum at this instant must also be given. Since in elementary physics mass is assumed to be constant momentum is proportional to the velocity and, hence, it may seem that it matters little which of the two is used. However, it must be emphasized that the generalized momenta used in Hamiltonian equations are very different from the mass—velocity products of elementary mechanics.

The state of a particle at any time is given by the pair of values  $(q, p) = (\text{position, momentum})$  determined by the differential equations of dynamics [Eq. (4.1)]. As the point moves on a straight line, the values of number pair  $(q, p)$  will change. Quasi-geometrical terminology makes for convenient and lucid expression and considerably facilitates the study of the changes in the state as time goes on. Any number pair can be plotted as the rectangular coordinates of a point in a Cartesian graph (Fig. 4.2).

Every such point which corresponds to a certain value of coordinate  $q_i$ , and momentum  $p_i$  of the system, describes both the position and momentum of the system at a particular instant, and hence represents a certain state of the system.

There will be different points for different states. As the particles moves on the straight line, its momentum and coordinate vary in accordance with Hamilton’s equation [Eq. (4.1)]. Its evolution through the successive states will be represented by a trajectory in the Cartesian plane (Fig. 4.3).

The state of the system when represented in this way is referred to as its *phase*, the representative point as the *phase point*, the trajectory as the *phase path* and the Cartesian plane as the *phase space*.

It is not necessary to start with Cartesian coordinates. Polar cylindrical or any other suitably defined set of coordinates would do as well. Nevertheless, we shall find that the phase space with rectangular axes corresponding to each coordinate and momentum is very convenient, as it has simple properties.

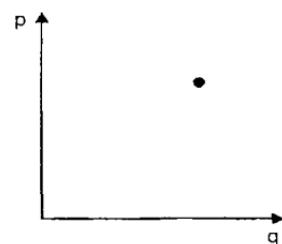


Fig. 4.2

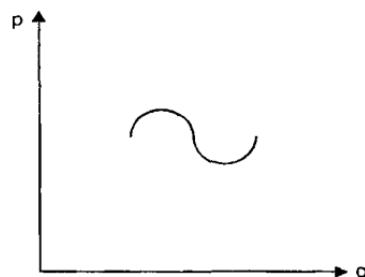


Fig. 4.3

**Example 4.1** Determine the phase trajectory of a bullet of unit mass fired straight upwards with an initial speed of 392m/s. Acceleration due to gravity is approximately 9.8m/s<sup>2</sup> or,

$$\frac{dv}{dt} = -9.8$$

Therefore  $v = -9.8 t + C_1$  (a constant)

From boundary conditions viz.

$$v = 392 \text{ when } t = 0, C_1 = 392$$

Therefore

$$v = 9.8 t + 392 \quad \dots(4.2)$$

$$p = mv = -9.8 t + 392 \quad (\text{because } m = 1) \quad \dots(4.3)$$

Now  $v = \frac{dq}{dt} = -9.8 t + 392$

On integrating  $q = -4.9 t^2 + 392 t + C_2$  (a constant)

Again, using intial conditions  $q = 0$  when  $t = 0, C_2 = 0$

$$\text{Therefore, } q = -4.9t^2 + 392 t \quad \dots(4.4)$$

Equations (4.3) and (4.4) give the pair values of the phase point at different times. Thus

(a) when	$t = 0,$	$q = 0,$	$p = 392$
(b) when	$t = 10,$	$q = 3430,$	$p = 294$
(c) when	$t = 30,$	$q = 7350,$	$p = 98$
(d) when	$t = 40,$	$q = 7840,$	$p = 0$
(e) when	$t = 60,$	$q = 5880,$	$p = -196$
(f) when	$t = 80,$	$q = 0,$	$p = -392$

If we plot these points as shown in Fig. 4.4, we get the phase space trajectory for the phase point of the bullet. The trajectory is obviously a parabola, the equation of which can be obtained by eliminating  $t$  between Eqs. (4.3) and (4.4) i.e.

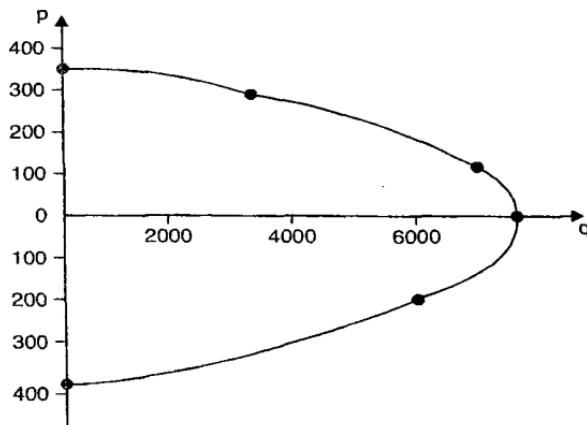


Fig. 4.4

$$q = -\frac{p^2}{196} + \frac{(392)^2}{19.6}$$

or  $p^2 + 19.6 q - 153664 = 0 \quad \dots(4.5)$

**Example 4.2** A particle of unit mass is executing simple harmonic vibrations. Determine its trajectory in phase space.

The total energy of the particle  $E$  which is constant of motion is given by

$$E = \frac{p^2}{2} + \frac{1}{2} kq^2 \quad \dots(4.6)$$

where the first term represents its kinetic energy and the second its potential energy.

The above equation can be written as

$$\frac{p^2}{2E} + \frac{q^2}{2E/k} = 1 \quad \dots(4.7)$$

The changes in  $q, p$  will always be subject to this condition. Equation (4.7) is the equation of the curve representing the successive states (phase) of the vibrating system. The equation represents an ellipse (Fig. 4.5) with semi-axes equal to  $\sqrt{2E}$  and  $\sqrt{2E/k}$ . Any point on the ellipse represents the phase  $(q, p)$  at some time, and the ellipse is described over and over again, since the particle is vibrating periodically in a straight line, representing the same positions and momenta.

For a given pair  $(q, p)$  the Eqs. (4.1) determine uniquely the rate of change of every coordinate in phase space. It follows at once that through every point in phase space, there passes but one trajectory. Hence, the representative point can never cross its previous path.

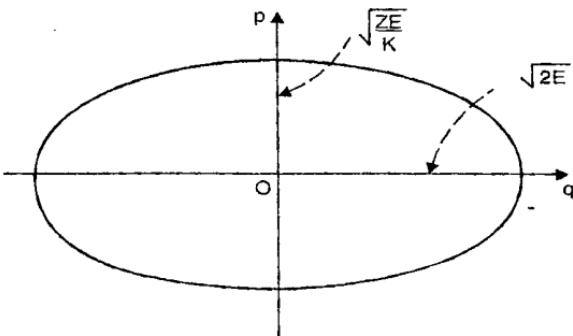


Fig. 4.5

Thus, the locus of a representative point in phase space is either a simple closed curve, or a curve that never intersect itself.

In the two examples that we have considered, it may be noted, that the actual motion of the system takes place in a straight line. The parabola

in the first example and ellipse in the second, is only the progress chart, not the actual path of the moving particle.

#### 4.4 THE $\mu$ -SPACE

A mechanical system slightly more advanced than a particle moving in a straight line, is a monatomic molecule moving in space. In a three-dimensional configuration space, the position of molecule is determined by the coordinates  $x, y, z$ . These coordinates, however, do not say anything about its motion. If instead, we imagine a three-dimensional space in which the coordinates are the momentum projections  $p_x, p_y, p_z$ , a momentum space, a point in it determines the state of motion of the molecule, but nothing about its position. A very meaningful way to determine the complete state of a molecule would be to set up a six-dimensional space with coordinates  $x, y, z, p_x, p_y, p_z$  in which every point represents a state of the molecule. Such a six dimensional space for a single particle is called its  $\mu$ -space. Note that phase space is purely a mathematical concept.

Suppose that the position or momentum of one of the molecules is changed slightly. The point of this molecule will undergo a displacement in the phase space, and the microscopic state of the gas will be modified. However, if the changes in the position and momentum of the molecule so slight that even the most accurate experiment would be unable to reveal them, we should assume that no change in the microscopic state has occurred.

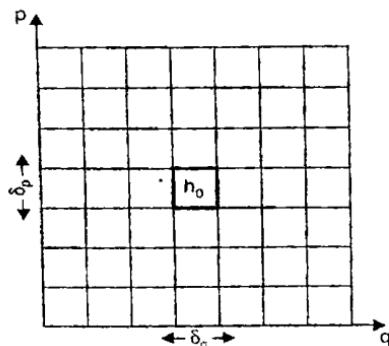


Fig. 4.6

Graphical representation of the foregoing is easily obtained. Consider a two-dimensional case. We subdivide the range of variables  $q$  and  $p$  into arbitrarily small discrete intervals. Let  $\delta q$  be the size of the intervals on the  $q$ -axis and  $\delta p$ , the corresponding size on the  $p$ -axis. Phase space is thus divided into small cells of equal area  $= \delta q \delta p = h_0$  (say) (Fig. 4.6). The state of the system can then be specified by stating that the representative point lies in a particular cell of phase space. In classical description  $h_0$  can be chosen arbitrarily small and the specification of state becomes

more and more precise, as we choose smaller and smaller magnitudes for  $h_0$ . It may be noted that  $h_0$  has the dimension of energy  $\times$  time. The lengths  $\delta q$  and  $\delta p$  are assumed to be so small that if a phase-point within a cell is slightly displaced to any point within the cell, the change in the position and the momentum will be too minute to be disclosed even by accurate measurements. If the particles is in the cell, its state is represented by the pair of coordinates  $(q_i, p_i)$ . If there is a change in the state of the particle it will move from this cell to another appropriate cell.

## 4.5 THE G-SPACE

For a system with  $n$  atoms a set of  $6n$  members  $(q_1, q_2, \dots, q_{3n}, p_1, p_2, \dots, p_{3n})$  is required to represent a phase point. Such a  $6n$ -dimensional space is called  $\Gamma$ -space. This is evidently built up of  $n$  spaces of  $\mu$ -type. It is also sometimes more convenient to regard  $\Gamma$ -space as constructed out of the *configuration space* that corresponds to a set of  $3n$  momenta conjugate to the coordinates.

In  $6n$ -dimensional case, we imagine, as in the two-dimensional case, the phase space to be partitioned into tiny juxtaposed 6-dimensional cells. These cells are all equal, the edges of the cells being of equal magnitude. We define an element of volume in Euclidean space  $dv = dx dy dz$  so that a system with coordinates within the range between  $x$  and  $x + dx$ ,  $y$  and  $y + dy$ ,  $z$  and  $z + dz$  lies within it. Analogously, a volume element in  $6n$ -dimensional phase space is expressed as

$$\begin{aligned} d\Gamma &= dq_1 dq_2 \dots dq_{3n} dp_1 dp_2 \dots dp_{3n} \\ &= h_0^{3n} \end{aligned} \quad \dots(4.8)$$

and the state of the system can be specified by starting in which particular cell the coordinates  $q_1, q_2, \dots, q_{3n}, p_1, p_2 \dots, p_{3n}$  of the system are found. The succession of states will be represented by trajectory in the  $6n$ -dimensional space. Such a space is difficult to visualise. It is purely a mathematical concept. In general, therefore, one deals with abstract paths in an abstract space.

It will be observed that the  $f$ -dimensional hyper volume in the phase space has the dimensions of  $(\text{energy} \times \text{time})^f$ . These dimensions hold regardless of the coordinates used. It can also be shown that on change of variable any given hyper volume goes over to a hyper volume of equal size in the new phase space (Prob. 4.3).

In Boltzmann's days there was no theoretical reason to ascribe any specific value  $h$  to the volume element in the phase space. But with the discovery of the Planck constant and the advent of quantum-theory, more light was thrown on the situation. We see that the assumption  $\delta q \delta p = h$  is now consistent with the Heisenberg uncertainty relation. According to this relation, if the position of a particle is uncertain within a volume  $dx dy dz$ , the momentum components of the particle are uncertain within a volume  $dp_x, dp_y, dp_z$  of momentum space. Consequently, all particles

situated in the special volume  $dx dy dz$  are indistinguishable. And between these two volumes we have the relation

$$dx dy dz dp_x dp_y dp_z = h^3 \quad \dots(4.9)$$

## 4.6 POSTULATE OF EQUAL A PRIORI PROBABILITIES

As stated in Chapter 2, it is convenient to analyze various problems in statistical physics, if we follow the method of *ensembles*. A vessel containing an ideal gas is a statistical system. An aggregate of such identical systems such as above is called a *statistical ensemble*, following the original terminology of Gibbs, one of the founders of statistical mechanics. Since the systems of the ensemble are identical their macroscopic states are the same, but microscopic states may be different.

Consider a system composed of  $N$  identical particles in a volume  $V$ ,  $n_1$  of which are with energy  $\varepsilon_1$ ,  $n_2$  with energy  $\varepsilon_2$  etc. If the particles are non-interacting the total energy is given by

$$E = \sum_i n_i \varepsilon_i \quad \text{and} \quad N = \sum_i n_i \quad \dots(4.10)$$

The specification of the actual values of the parameters  $E, V, N$  then defines a particular 'macrostate' of the given system. Since the total energy  $E$  consists of a simple sum of energies  $\varepsilon_i$ , there will obviously by a large number of different ways in which the individual  $\varepsilon_i$  can be chosen, so as to make the total energy  $E$ . In other words, there will be a large number of different ways in which the total energy equal to  $E$  of the system can be distributed among the  $N$  particles constituting it. Each of these different ways specifies a particular microstate of the given system. In any case, to a given macrostate of the system there does, in general, correspond a large number of microstates and it seems natural that at any time  $t$ , the system is equally likely to be in any one of these microstates. That is, all microstates are equally probable. This is generally referred to as the '*principal of equal a priori probability*'. This principal can be considered as the basis of the entire theory of systems in equilibrium. If all the microscopic states have the same probability, the probability of a given macroscopic state will be proportional to the number of different states which it contains.

## 4.7 ERGODIC HYPOTHESIS

In statistical mechanics we have often to deal with the average or the mean of a quantity. The average of a physical quantity can be determined in two ways: (i) one could consider an ensemble of a large number of identical systems and average, the physical quantity over all these systems at one instant of time to determine its *ensemble average*; or (ii) a system could be followed over a very long period of time, during which the system takes different values. The average of the physical quantity over the long periodic gives the *time averaged value* of the quantity.

Ergodic hypothesis is that these two averages are identical:

#### 4.7.1 Mean Value Over an Ensemble

Suppose we are interested in the mean value of the square of the coordinate of a particle. Let  $N$  be the number of identical systems in the ensemble and  $q_i$  the coordinate of the particle in the  $i$ th system. The mean value of the square of the coordinate is given by

$$\langle q^2 \rangle_e = \frac{1}{N} \sum_i q_i^2 \quad \dots(4.11)$$

The subscript  $e$  indicates that the mean is taken over the entire ensemble. A particle may appear in a particular cell in a number of systems. Let  $N_j$  be the number of systems in which the particle is found in the  $j$ th cell with coordinate  $q_j$ . The contribution by  $N_j$  cells to  $\sum_i q_i^2$  is  $N_j q_j^2$ . Grouping together the terms corresponding to the same cell in different systems, we can write

$$\sum_{i=1}^N q_i^2 = \sum_j N_j q_j^2 \quad \dots(4.12)$$

where the summation is taken over all the cells of each system. Using this we can express Eq. (4.11) in the form

$$\begin{aligned} \langle q^2 \rangle_e &= \frac{1}{N} \sum_{i=1}^N q_i^2 \\ &= \frac{1}{N} \sum_j N_j q_j^2 = \sum_j \frac{N_j}{N} q_j^2 \end{aligned} \quad \dots(4.13)$$

By definition, the probability that the particle is in the  $j$ th cell is

$$P_j = \frac{N_j}{N} \quad \dots(4.14)$$

$$\text{Hence } \langle q^2 \rangle_e = \sum_j P_j q_j^2 \quad \dots(4.15)$$

#### 4.7.2 Mean Value Over Time

Let us now concentrate on a single of the ensemble. The coordinate of the particle changes with time as the particle jumps from cell to cell. We keep the particle under observation for a very long time. The mean of the square of the coordinate is then given by

$$\langle q^2 \rangle_t = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T q^2(t) dt \quad \dots(4.16)$$

Here, the subscript  $t$  indicates that the mean is taken over time, and  $T$  is the total time during which observations have been made. The particle jumps from cell to cell during the time of observation. Let  $m$  be the

number of jumps during time  $T$ . Suppose in the  $i$ th jump the particle is in a cell with coordinate  $q_i$  and its duration in this cell is  $\Delta t_i$ .

Therefore  $\sum \Delta t_i = T$

$$\text{and } \sum_{i=1}^m q_i^2 \Delta t_i = \int_0^T q^2(t) dt \quad \dots(4.17)$$

We can express this relation in a different form. During a very long time, the particle arrives in each cell several times. Let  $m_j$  be the number of times it arrives in the  $j$ th cell, its coordinates being  $q_j$  and its duration in this cell  $\Delta t_j$ . Equation (4.17) now can be expressed as

$$\begin{aligned} \int_0^T q^2(t) dt &= \sum_{i=1}^m q_i^2 \Delta t_i = \sum_{j=1}^M q_j^2 m_j \Delta t_j \\ &= \sum_{j=1}^M q_j^2 T_j \end{aligned} \quad \dots(4.18)$$

where  $M$  is the total number of cells in a system and  $T_j = m_j \Delta t_j$  is the total duration of the stay of the particle in the  $j$ th cell.

Equation (4.16) now can be written as

$$\langle q \rangle_t^2 = \lim_{T \rightarrow \infty} \frac{1}{T} \sum_{j=1}^M T_j q_j^2 = \lim_{T \rightarrow \infty} \sum_{j=1}^M \frac{T_j}{T} q_j^2 \quad \dots(4.19)$$

Since out of the total time of observation  $T$ , the particle stays in the  $j$ th cell for the time  $T_j$ , the probability that the particle is in  $j$ th cell can be taken to be

$$\bar{P}_j = \lim_{T \rightarrow \infty} \frac{T_j}{T} \quad \dots(4.20)$$

Hence

$$\langle q \rangle_j^2 = \sum_{j=1}^M \bar{P}_j q_j^2 \quad \dots(4.21)$$

This formula is similar to Eq. (4.15). The question is whether the probability  $\bar{P}_j$  is equal to  $P_j$ . We have not proved it to be so, but intuitively they seem to be equal. The assumption that  $\bar{P}_j$  is the basis of what is known as *Ergodic hypothesis*, which can be expressed as

'The mean over the ensemble is equal to the mean over time,' i.e.

$$\langle q^2 \rangle_e = \langle q^2 \rangle_t \quad \dots(4.22)$$

This is one of the basic assumptions of statistical physics.

## 4.8 DENSITY DISTRIBUTION IN PHASE SPACE

Suppose the system in whose physical properties we are interested is a gas in a container. We then consider simultaneously a large number

(ensemble) of containers having the same shape and containing the same number of molecules of the gas of interest. The phases—the positions and momenta of the molecules at a particular instant—vary from one container to another. The values of  $\{q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f\}$  at that instant are different for the different systems of the ensemble and they are represented by different points in the phase space. As time goes on, these different representative points will move describing the trajectories, each one of which will give the dynamic history of one system of the ensemble. The instantaneous state of any system in the ensemble can then be regarded as specified by the position of the representative point in the phase space, and the condition of the ensemble as a whole can be regarded as a 'cloud' of such representative points. One can imagine the phase points as a cloud of dust (in hyperspace) whose individual dust particles are in motion in accordance with dynamical laws. The density of this cloud at a particular place may vary as time goes on, or may appear to vary from place to place at a particular time. It must be emphasized here that the systems of an ensemble are independent system, that is, there is no interaction between them and hence the trajectories do not intersect.

Since in statistical physics we are interested in the number of systems at any time which would be found in the different states that correspond to different regions of the phase space, there is no need to maintain distinction between individual system. The condition at any time is described through a function  $\rho$  which represents the density of the probability distribution in the phase space. The function  $\rho$  gives the number of states per unit volume of the phase space. It is therefore necessary to formulate the family of probability density functions for the states of the systems of the ensemble at different times. We will, thus, set up the machinery for a microscopic probabilistic description of matter.

Given a real  $N$ -particle system, we never know exactly what its state is. We can only say with a certain probability that it is one of the points in the phase space. We can, thus, assign a probability distribution to the points in phase space, which can be regarded as a probability fluid which flows according to Hamiltonian dynamics.

The density distribution function is obviously a function of the coordinates  $q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f$ , and time. Thus, the density distribution function may be represented by  $\rho(q_1, \dots, q_f, p_1, \dots, p_f, t)$  or briefly by  $\rho(q, p, t)$ . Therefore, the number of phase points (or systems) in a small volume element  $d\Gamma = dq_1, \dots, dp_f$  is given by

$$\delta N = \rho(q, p, t) dq_1 \dots dq_f dp_1 \dots dp_f \quad \dots(4.23)$$

and 
$$N = \sum \rho(q, p, t) dq_1 \dots dq_f dp_1 \dots dp_f \quad \dots(4.24)$$

If the population  $N$  is assumed to be very large,  $\rho$  and  $\delta N$  can be regarded as varying continuously and, hence, the total number of systems  $N$  is given by

$$N = \int \dots \int \rho(q, p, t) dq_1 \dots dq_f dp_1 \dots dp_f \quad \dots(4.25)$$

The knowledge of the distribution would be sufficient to determine the average values of different mechanical properties of the system comprising the ensemble. From the definition of probability, we see that the probability per unit volume of finding the phase point for a system in

different regions of space is  $\frac{\rho(q, p, t)}{N}$ . If the properties of an ensemble

are known as functions of the position  $q, p$  in  $\Gamma$ -space, then the average properties of the ensemble will be found by averaging the known functions over all allowed positions  $q, p$ . Thus if  $\chi(q, p)$  is a measurable property characterizing the system, its mean value for all the systems in the ensemble would be given at time,  $t$ , by

$$\text{then } \langle \chi \rangle = \frac{\int \dots \int \chi(q, p) \rho(q, p) dq_1 \dots dp_f}{\int \dots \int \rho(q, p) dq_1 \dots dp_f} \quad \dots(4.26)$$

If  $\rho$  is normalized to unity i.e. if

$$\rho = \int \dots \int \rho(q, p) dq_1 \dots dp_f = 1$$

$$\langle \chi \rangle = \int \dots \int \chi(q, p) \rho(q, p) dq_1 \dots dp_f \quad \dots(4.27)$$

That is,  $\rho$  itself gives directly the probability per unit volume.

## 4.9 LIOUVILLE'S THEOREM

Let us now inquire into the rate of change of phase point density in a classical system.

Consider a small volume element in the hyperspace, bounded by  $q_1$  and  $q_1 + \delta q_1$ ,  $p_1$  and  $p_1 + \delta p_1$ , etc. The number of systems in the element using Eq. (4.23) is

$$\delta N = \rho d \Gamma = \rho(q, p, t) \delta q_1 \dots \delta p_f$$

The motion of every system is governed by Hamilton's equations. Representative points will enter and leave through the boundary surfaces of the element. Since the number of phase points entering the element of hyper volume through any 'face' will in general be different from the number of points which are leaving the opposite 'face', the number  $\delta N$

will be changing. The change is equal to  $\frac{\partial \rho}{\partial t} dt \delta q_1 \dots \delta p_f$ . We can construct

a conceptual Euclidean space of  $2f$  dimensions. Consider two faces perpendicular to the  $q_1$ -axis which are located at  $q_1$  and  $q_1 + \delta q_1$ . The number of phase points entering the element in time  $dt$  through the face  $q_1 = \text{constant}$  is (Fig. 4.7).

$$= \rho(q, p, t) \dot{q}_1 dt \delta q_2 \dots \delta p_f \quad \dots(4.28)$$

where  $\dot{q}_1$  is the velocity in the direction  $q_1$ .

The number leaving the element through the face  $q_1 + \delta q_1 = \text{constant}$  is

$$= \left[ p\dot{q}_1 + \frac{\partial}{\partial q_1} (p\dot{q}_1) \delta q_1 \right] dt \delta q_2 \dots \delta p_f \quad \dots(4.29)$$

Hence, the effective number of systems entering the element in the direction  $q_1$  is

$$\begin{aligned} &= p\dot{q}_1 dt \delta q_2 \dots \delta p_f - \left[ p\dot{q}_1 + \frac{\partial}{\partial q_1} (p\dot{q}_1) \delta q_1 \right] dt \delta q_2 \dots \delta p_f \\ &= - \frac{\partial}{\partial q_i} (p\dot{q}_i) dt \delta q_1 \delta q_2 \dots \delta p_f \quad \dots(4.30) \end{aligned}$$

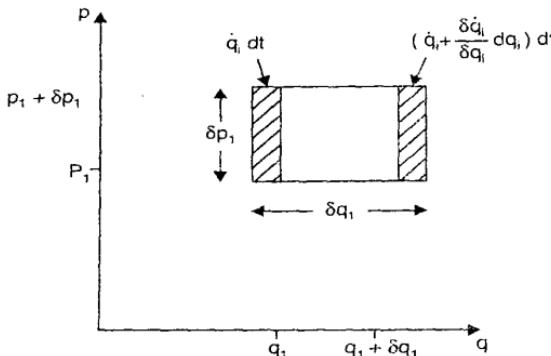


Fig. 4.7

Therefore, the net number entering the volume element through all its faces is given by

$$\frac{\partial p}{\partial t} dt \delta q_1 \dots \delta p_f = \left[ - \sum_{i=1}^f \frac{\partial}{\partial q_i} (p\dot{q}_i) - \sum_{i=1}^f \frac{\partial}{\partial p_i} (p\dot{p}_i) \right] dt \delta q_1 \dots \delta p_f$$

We, thus obtain the relation

$$\frac{\partial p}{\partial t} = - \sum_{i=1}^f \left[ \frac{\partial}{\partial q_i} (p\dot{q}_i) + \frac{\partial}{\partial p_i} (p\dot{p}_i) \right] \quad \dots(4.31)$$

This result can be simplified to yield

$$\frac{\partial p}{\partial t} = - \sum_{i=1}^f \left[ p \left( \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) + \left( \frac{\partial p}{\partial q_i} \dot{q}_i + \frac{\partial p}{\partial p_i} \dot{p}_i \right) \right] \quad \dots(4.32)$$

From Hamilton's equation of motion

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial}{\partial q_i} \frac{\partial H}{\partial p_i} = \frac{\partial^2 H}{\partial q_i \partial p_i}$$

$$\frac{\partial \dot{p}_i}{\partial p_i} = - \frac{\partial}{\partial p_i} \frac{\partial H}{\partial q_i} = - \frac{\partial^2 H}{\partial q_i \partial p_i}$$

Therefore, the first term in the bracket vanishes and

$$\left( \frac{\partial \rho}{\partial t} \right)_{q,p} = - \sum_{i=1}^f \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \quad \dots(4.33)$$

The symbol of partial differentiation indicates that  $\left( \frac{\partial \rho}{\partial t} \right)_{q,p}$  gives the rate of the change in density at the point of interest. This is known as *Liouville's equation* and is of fundamental importance in statistical mechanics.

It is easy to see that the equation can be written in any of the following forms:

$$(i) \quad \frac{\partial \rho}{\partial t} + \sum_{i=1}^f \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0 \quad \dots(4.34)$$

$$(ii) \quad \frac{\partial \rho}{\partial t} + \sum_{i=1}^f \left( \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) = 0 \quad \dots(4.35)$$

$$(iii) \quad \frac{\partial \rho}{\partial t} + \{ \rho, H \} = 0 \quad \dots(4.36)$$

where

$$\{ \rho, H \} = \sum_i \left( \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right)$$

is known as the Poisson bracket of the functions  $\rho$  and  $H$ .

The total time derivative of  $\rho (q, p, t)$  is given by

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^f \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0 \quad \dots(4.37)$$

In other words the density of phase points is an integral of motion. This is *Liouville's theorem* in classical presentation.

## 4.10 PRINCIPLE OF CONSERVATION OF DENSITY IN PHASE AND PRINCIPLE OF CONSERVATION OF EXTENSION IN PHASE

Equation (4.36) shows that the density does not change if one moves in the phase space along with the point representing a system; that is, the density does not change with time in the neighbourhood of any selected moving point in the  $\Gamma$ -phase space. Thus, in a given region

$$\delta V = \delta q_1 \delta q_2 \dots \delta q_v \delta p_1 \delta p_2 \dots \delta p_v$$

on the  $\Gamma$ -space there will be

$$\delta N = \frac{\delta q_1 \dots \delta p_v}{h^v} \quad \dots(4.38)$$

states, where  $v$  is the number of degrees of freedom. According to Eq. (4.37) this number will always remain the same, irrespective of what coordinates we use to describe the system. Hence, the distribution of representative points moves in the  $\Gamma$ -space like an incompressible fluid. Gibbs referred to this fact as the *principle of conservation of density in phase*.

We can arrive at yet another important principle from Liouville's theorem. Consider a region  $\delta V$  in a phase space, small enough so that the density  $\rho$  is uniform over its extent. Boundaries of the region are permanently determined by representative points lying in it. The number of elements in this region is

$$\delta N = \rho \delta V$$

In the course of time, each point in this region traces out a trajectory in phase space. Hence, at a latter time  $t_1$ , the region  $\delta V$  will have gone to a new region  $\delta V'$  of the phase space. Both  $\delta V$  and  $\delta V'$  contain the same number of states and, hence, they must have the same volume in phase, although their shapes may be different. This can be proved as follows:

As no representative point can cross the boundary, nor can any point be created or destroyed,

Therefore

$$\begin{aligned} \frac{d}{dt}(\delta N) &= \frac{d}{dt}(\rho \delta V) = \frac{d\rho}{dt} \delta V + \rho \frac{d}{dt}(\delta V) = 0 \\ \text{or } \frac{d}{dt}(\delta V) &= 0 \text{ (because } \frac{d\rho}{dt} = 0) \\ \text{i.e. } \frac{d}{dt} \int \dots \int \delta q_i \dots \delta p_f &= 0 \end{aligned} \quad \dots(4.39)$$

Thus, if a given number of representative points occupy an element of volume  $\delta V$  at a certain time, they will occupy another volume of equal size at a later time, although the volume element may change its shape. This is known as the *principle of conservation of extension*.

## 4.11 CONDITION FOR STATISTICAL EQUILIBRIUM

Liouville's fundamental theorem which controls the temporal behaviour of ensembles, permits us to discuss the conditions for statistical equilibrium.

The ensemble is considered to be in statistical equilibrium if  $\rho$  has no explicit dependence on time at all points in phase space, i.e.

$$\frac{\partial \rho}{\partial t} = 0 \quad \dots(4.40)$$

Under the condition of equilibrium therefore, by Eq. (4.32)

$$\sum_{i=1}^f \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0 \quad \dots(4.41)$$

This equation will be satisfied if  $\rho$  is independent of coordinates  $(q, p)$  i.e.

$$\rho(q, p) = \text{constant} \quad \dots(4.42)$$

In other words, representative points are uniformly distributed in the phase space.

More generally, under statistical equilibrium, the density must be a function of the constants of motion only. Thus, if  $\alpha$  is a constant of motion,  $\rho = \rho(\alpha)$ , so that

$$\frac{\partial \rho}{\partial t} = \frac{\partial \rho}{\partial \alpha} \frac{\partial \alpha}{\partial t} = \frac{\partial \rho}{\partial \alpha} \sum_{i=1}^f \left( \frac{\partial \alpha}{\partial q_i} \dot{q}_i + \frac{\partial \alpha}{\partial p_i} \dot{p}_i \right) = 0 \quad \dots(4.43)$$

It may be noted that when the system is in statistical equilibrium the observed values of the macroscopic physical quantities are to a high degree of accuracy, equal to their mean values.

## PROBLEMS

- 4.1 A system of 4 particles has energy levels with energies 0, 1, 2, 3 units. The total energy of the system is 3 units. List the accessible microstates, if the particles are (i) indistinguishable (ii) distinguishable.
- 4.2 Discuss the nature of the trajectory in the phase space of a simple pendulum. Show that the area enclosed by the trajectory is equal to the product of the total energy  $E$  and the time period  $T$ .
- 4.3 Show that the element  $d\Gamma$  of the phase space of a single particle is invariant under the transformation from the Cartesian coordinates to the spherical polar coordinates.
- 4.4 Find the phase trajectory for a particle of mass  $m$  and charge  $-e$ , moving under the influence of a Coulomb force of attraction towards a fixed charge  $+e_i$  at a distance  $r_0$ .
- 4.5 A linear harmonic oscillator is described by the equation

$$\ddot{x} + \gamma \dot{x} + \omega^2 x = 0; \omega = \sqrt{\frac{k}{m}} : \gamma \ll \omega$$

Determine and draw its phase trajectory.

- 4.6 The movement of phase points may be regarded as a steady flow of a 'gas' in phase space of  $2f$  dimensions. Obtain Liouville's equation, starting from the equation of continuity applicable for fluids.
- 4.7 Verify Liouville's theorem in the case of the motion of three particles in a constant gravitational field, the initial states of the particles being given by the phase points.

$$A(p_0, Z_0), B(p_0, Z_0 + l), C(p_0 + b, Z_0)$$



In the formulation of statistical mechanics, Gibbs introduced three standard ensembles to which real experiments could be approximated. These are: (i) the microcanonical ensemble, (ii) the canonical ensemble and (iii) the grand canonical ensemble. Their classification depends on the manner in which their systems interact. Each of them has its own characteristics distribution. Physical systems can interact in a variety of ways; in particular, they may exchange energy, or matter or both with each other. The ensemble in which the systems exchange energy but not matter, is called a *canonical ensemble*, that in which both energy and matter are exchanged between the systems is called a grand *canonical ensemble*; and that in which neither energy nor matter is exchanged, is called a *microcanonical ensemble*. Statistical mechanics provides a number of methods for calculating equilibrium thermodynamic properties of macroscopic systems. Explicit calculations of thermodynamics functions can be carried out using microcanonical, canonical or grand canonical ensembles. A specific choice of ensembles may be thought of as corresponding to a particular physical situation.

### 5.1 MICROCANONICAL ENSEMBLE

This ensemble consists of systems which are isolated from the rest of the world. Such a system is also known as a 'closed isolated system' and has a fixed volume, fixed total energy and a fixed total number of particles. The probability density  $P(p, q)$  of such a system differs from zero only on the constant energy hypersurface. It must be noted, however, that in reality one cannot achieve complete isolation of a system. We must allow for some interaction energy  $\Delta E$ , though very small. The elements of the microcanonical ensemble, therefore, lie within the range between  $E$  and  $E + \Delta E$ .

The picture of a microcanonical distribution in phase space would be something like a very thin uniform cloud. One can easily see this by referring to Fig. 5.1, which gives the trajectory of a simple harmonic oscillator. The ellipse  $E$  represents the evolution of our conservative system with total energy  $E$ . This system is just one member of the ensemble. The other members may have energy between  $E$  and,  $E + \delta E$ .

and hence their corresponding phase points will be between two ellipses. The thin elliptic cloud is the energy shell. If we conceive of  $\delta E$  as getting smaller and smaller, the energy shell between the two surfaces would become just a surface in the limit as  $\delta E \rightarrow 0$ .

According to the fundamental postulate of equal a priori probability under the condition of equilibrium the system is equally likely to be found in one of its accessible states. In the case of microcanonical ensemble all states between  $E$  and  $E + \delta E$  are equally accessible. Therefore, if the

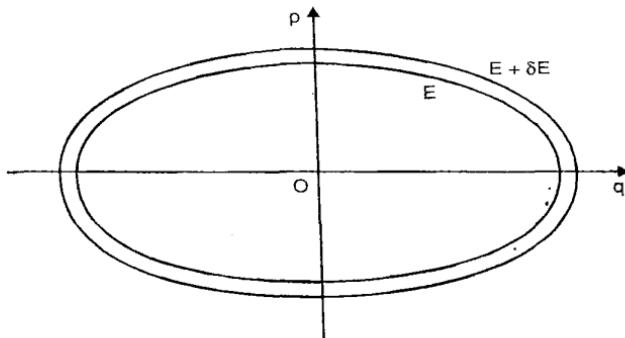


Fig. 5.1

system is in a state  $X$ , corresponding to the energy  $E_x$ , the probability  $P_x$  of finding the system in state  $X$  is given by

$$P_x = \begin{cases} C & \text{if } E < E_x < E + \delta E \\ 0 & \text{otherwise} \end{cases} \quad \dots(5.1)$$

where  $C$  is a constant, the value of which can be determined from the normalization condition  $\sum P_x = 1$ , when summed over all accessible states in the range between  $E$  and  $E + \delta E$ . It should be more appropriate to write this relation as  $P_x = C \delta(E - E_x)$ , where  $\delta$  is the Dirac delta function.

## 5.2 CANONICAL ENSEMBLE

It is evident that the microcanonical ensemble is fundamental and refers to the simple situation in which the constituent system are isolated and not influenced in any way by external disturbances. One would, therefore, think it proper to use such ensembles in the development of the basic theory. However, as pointed out above, microcanonical ensembles are best suited for isolated systems, and we seldom deal with a completely isolated system; there is always some energy exchange with surroundings. It would be more realistic, therefore, to use an ensemble in which statistical equilibrium is attained not by isolation but by free interaction. Canonical ensembles have been found to be more appropriate

for the description of such systems. Besides, canonical approach gives results which apply even when components interact strongly.

Suppose we desire to study the statistical properties of a thermodynamical system  $A$ . To this end we envisage an assembly of a very large number of systems ( $N$ ) identical in volume and molecular composition with  $A$ . Each system of the assembly is considered to be in thermal contact with a huge heat reservoir. A heat reservoir is a system whose heat capacity is so much higher than that of the subsystem in contact with it, that heat flow from or to the heat reservoir does not change its temperature significantly. The assembly can be thought of as contained within a microcanonical ensemble. Each system of the assembly is in contact with the other elements of the microcanonical ensemble, but is otherwise isolated from the outside world. The walls of the containers of the system of the assembly which separate it from microcanonical ensemble are *diathermic* walls, which allow heat to flow through them but do not allow the exchange of mass. An assembly of this kind is called a *canonical ensemble* of systems of type  $A$ . The number of systems in a canonical ensemble is constant; but their energy is not fixed.

Let us now find the probability that a canonical system, under the condition of equilibrium, is in a particular state with specific energy  $E_\alpha$ .

Consider a canonical system  $A$  in a microcanonical ensemble  $A'$  ( $A \ll A'$ ) (Fig., 5.2). The walls of  $A$  are such that  $A$  and  $A'$  are free to exchange energy. The microcanonical ensemble is isolated and its total energy  $E_0$  is constant. As discussed before, a large number of microscopic states correspond to the macroscopic state of the microcanonical ensemble with energy  $E_0$ . Let  $\Omega_0$  be the total number of microstates of the microcanonical ensemble with energy  $E_0$ . By the postulate of equal a priori probability, all these microstates are

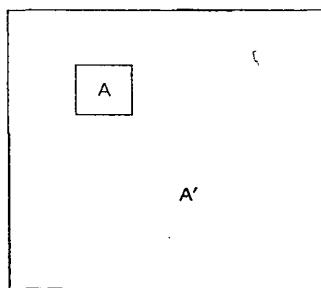


Fig. 5.2

equally probable. Therefore, the probability of each microstate is  $\frac{1}{\Omega_0}$ . It

is obvious that different microstates of the microcanonical ensemble  $A'$  will give rise to different microstates of the small subsystem  $A$ . Suppose, a certain microstate of  $A'$  gives rise to a microstates of  $A$  with energy  $E_\alpha$  ( $E_\alpha \ll E_0$ ). Hence, the energy of the remaining part of the complete system is  $E_0 - E_\alpha$ . This is one microstate of  $A$  with energy  $E_\alpha$ , attained through the other microstates of  $A'$ . Let the number of states of the microcanonical ensemble  $A'$ , through which the states of the small system  $A$  corresponding to the energy  $E_\alpha$  are attained, be  $\Omega_\alpha(E_0 - E_\alpha)$ . Therefore, the probability that the small system  $A$  is in a state with energy  $E_\alpha$  is

$$P_\alpha = \frac{\Omega_\alpha(E_0 - E_\alpha)}{\Omega_0} \quad \dots(5.2)$$

Using the relation

$$\alpha = e^{\ln \alpha}$$

we can express Eq. (5.2) as

$$P_\alpha = \frac{e^{\ln \Omega_\alpha(E_0 - E_\alpha)}}{\Omega_0} \quad \dots(5.3)$$

Expanding  $\ln \Omega_\alpha(E_0 - E_\alpha)$  into a Taylor's series

$$\ln \Omega_\alpha(E_0 - E_\alpha) = \ln \Omega_\alpha(E_0) - E_\alpha \frac{\partial \ln \Omega_\alpha(E_0)}{\partial E_0} + \text{higher order terms} \quad \dots(5.4)$$

Putting  $\beta = \frac{\partial \ln \Omega_\alpha(E_0)}{\partial E_0}$  and neglecting higher order terms

$$\ln \Omega_\alpha(E_0 - E_\alpha) = \ln \Omega_\alpha(E_0) - \beta E_\alpha$$

Hence

$$\begin{aligned} P_\alpha &= \frac{e^{\{\ln \Omega_\alpha(E_0) - \beta E_\alpha\}}}{\Omega_0} = \frac{e^{\ln \Omega_\alpha(E_0)}}{\Omega_0} e^{-\beta E_\alpha} \\ &= \frac{\Omega_\alpha(E_0)}{\Omega_0} e^{-\beta E_\alpha} = \text{const.} \times e^{-\beta E_\alpha} \end{aligned} \quad \dots(5.5)$$

From the normalization condition  $\sum P_\alpha = \text{const.} \times \sum e^{-\beta E_\alpha} = 1$

$$\text{Therefore, } \text{const.} = \frac{1}{\sum e^{-\beta E_\alpha}} \quad \dots(5.6)$$

$$\text{and } P_\alpha = \frac{e^{-\beta E_\alpha}}{\sum e^{-\beta E_\alpha}} \quad \dots(5.7)$$

This is the Gibbs *canonical distribution*. It gives the probability that the small system A be in a state with energy  $E_\alpha$ . There may be other microstates of A with the same energy  $E_\alpha$ . If this number is  $g_\alpha$ .

$$P_\alpha = \frac{g_\alpha e^{-\beta E_\alpha}}{\sum e^{-\beta E_\alpha}} \quad \dots(5.8)$$

The denominator is usually represented by  $Z$ , i.e.

$$Z = \sum_\alpha e^{-\beta E_\alpha} \quad \dots(5.9)$$

$$\text{Therefore } P_\alpha = \frac{g_\alpha e^{-\beta E_\alpha}}{Z} \quad \dots(5.10)$$

If  $E$  is a continuous variable

$$Z = \int_0^\infty e^{-\beta E} dE_\alpha \quad \dots(5.11)$$

We have yet to identify the parameter  $\beta$ , which we will shortly do. Meanwhile, we shall discuss here an example which gives a clue towards the identification of  $\beta$ .

Consider a composite system  $A^0$  made up of two systems  $A$  and  $A'$  in thermal contact and weakly interacting with each other. Let  $A$  be in a state  $r$  with energy  $E_r$  and  $A'$  in a state  $s$  with energy  $E_s$ . The energy of the composite system  $A^0$ , therefore, is  $E^0 = E_r + E_s$ .

If the two systems are separately in internal equilibrium, the probabilities of finding them in respective states are given by

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}, \quad P_s = \frac{e^{-\beta^1 E_s}}{\sum_s e^{-\beta^1 E_s}} \quad \dots(5.12)$$

These probabilities are statistically independent. Therefore, the probability  $P_{rs}$  that the system  $A$  is in state  $r$  and  $A'$  in state  $s$  simultaneously, is given by the product of  $P_r$  and  $P_s$ :

$$P_{rs} = P_r P_s = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \cdot \frac{e^{-\beta^1 E_s}}{\sum_s e^{-\beta^1 E_s}} \quad \dots(5.13)$$

Evidently, this does not correspond to a canonical distribution of the composite system and, hence, does not describe an equilibrium situation. Exchange of energy between the two systems, therefore will continue until equilibrium is reached. The time taken by the systems to reach the state of equilibrium from its initial state of non-equilibrium is called relaxation time.

However if  $\beta = \beta^1$ . Eq. (5.13) reduces to

$$P_{rs} = \frac{e^{-\beta(E_r + E_s)}}{\sum_r \sum_s e^{-\beta(E_r + E_s)}} \quad \dots(5.14)$$

which corresponds to the canonical distribution.

Since the only criterion for thermodynamic equilibrium under these conditions is that the temperature of the two systems be equal, it is valid to assume  $\beta$  as a function of temperature.

### 5.3 ALTERNATIVE METHOD FOR THE DERIVATION OF CANONICAL DISTRIBUTION

Consider an ensemble consisting of a large number of systems  $N$ . As in the preceding section the system are separated by diathermic walls permit the transfer of energy from one to the other. Suppose now that

$n_1$  of these systems are in state 1 with energy  $E_1$ ,

$n_2$  of these systems are in state 2 with energy  $E_2$

$n_3$  of these system are in state 3 with energy  $E_3$

$n_i$  of these systems are in state  $i$  with energy  $E_i$  ...(5.15)

This is one of the modes of distributing the total energy  $E$  among  $N$  constituents of the ensemble. It is obvious that

$$\sum n_i = N; \quad \sum n_i E_i = N \langle E \rangle \quad \dots(5.16)$$

where  $\langle E \rangle$  stands for the average energy per system.

Any set of numbers  $(n_1, n_2, \dots, n_i)$  such as (5.15) which satisfies the restrictive condition given by Eq. (5.16) is a possible mode of distribution and any such mode can be realized in a number of ways by effecting a reshuffle among the members of the ensemble.

We will now find the probability for such a distribution to occur.

Let us first find the number of ways in which a distribution such as (5.15) can be obtained. Since, of the total number of  $N$  systems  $n_1$  are to be accommodated in state 1, the first can be chosen in  $N$  ways; the second in  $N - 1$  ways ... and  $n_1^{th} N - n_1 + 1$  ways.

Therefore, the total number of possible ways  $= N(N - 1) \dots (n - n_1 + 1)$

$$= \frac{N!}{(N - n_1)!} \quad \dots(5.17)$$

However,  $n_1$  systems in state 1 are distinguishable and, hence, permutations of these systems among themselves do not give a new mode of distribution. The number of possible permutations being  $n_1!$ , the total number of distinct ways in which  $n_1$  systems can be selected out of  $N$  is

$$\frac{N!}{n_1!(N - n_1)!}$$

We are now left with  $N - n_1$  systems, of which  $n_2$  are to be placed in state 2. This can be done in  $\frac{(N-1)!}{n_2!(N-n_1-n_2)!}$  ways.

Proceeding in this way we find that the number of ways in which the distribution such as (5.15) can be obtained is

$$\begin{aligned} &= \frac{N!}{n_1!(N - n_1)!} \times \frac{(N-1)!}{n_2!(N-n_1-n_2)!} \times \\ &\qquad\qquad\qquad \frac{(N-n_1-n_2)!}{n_3!(N-n_1-n_2-n_3)!} \times \dots \\ &= \frac{N!}{n_1!n_2!n_3!} \quad \dots(5.18) \end{aligned}$$

The probability  $W$  of obtaining such a distribution can be found from the ratio of this number to the total number of all possible distributions, say  $C$ :

$$\text{Therefore } W = \frac{1}{C} \frac{N!}{n_1!n_2!\dots} \quad \dots(5.19)$$

Accordingly, the most probable mode of distribution will be the one for which  $W$  is maximum.

Taking logarithms

$$\ln W = \ln N! - \sum_i n_i! - \ln C \quad \dots(5.20)$$

By Stirling's formula

$$\ln N! = N \ln N - N$$

$$\text{Therefore, } \ln W = N \ln N - N - \sum_i n_i \ln n_i + \sum_i n_i - \ln C$$

$$\ln W = N \ln N - \sum_i n_i - \ln n! - \ln C \quad \dots(5.21)$$

For  $W$  to be maximum  $\delta \ln W = 0$  i.e.

$$\delta \sum_i n_i \ln n_i = 0$$

$$\text{Therefore } \sum_i (\delta n_i + \ln n_i \delta n_i) = 0 \quad \dots(5.22)$$

The other restrictive conditions are

$$\sum_i n_i = N \text{ and } \sum_i \frac{n_i E_i}{N} = E$$

On taking differentials

$$\sum_i \delta n_i = 0; \quad \sum_i E_i \delta n_i = 0 \quad \dots(5.23)$$

Therefore, for  $W$  to be maximum

$$\sum_i \ln n_i \delta n_i = 0 \quad \dots(5.24)$$

subject to the conditions (5.23).

Following the technique of Lagrange's multipliers (see Appendix A), we multiply the first of Eq. (5.23) by  $\alpha$  and the second by  $\beta$  and add these to Eq. (5.24), to get

$$\sum_i (\ln n_i + \alpha + \beta E_i) \delta n_i = 0 \quad \dots(5.25)$$

If  $\alpha, \beta$  are chosen suitably,  $\delta n_i$  can be regarded as independent and, hence, the coefficient of each  $\delta n_i$  must vanish separately.

$$\text{Therefore } \ln n_i + \alpha + \beta E_i = 0 \quad \dots(5.26)$$

$$\text{or } n_i = e^{-\alpha - \beta E_i} = e^{-\alpha} e^{-\beta E_i} \quad \dots(5.27)$$

Since

$$\sum n_i = N$$

$$e^{-\alpha} \sum_i e^{-\beta E_i} N \quad \dots(5.28)$$

$$\text{and } n_i = \frac{N e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad \dots(5.29)$$

The probability of finding a system in state  $i$  is  $P_i = \frac{n_i}{N}$

$$\text{Therefore } P_i = \frac{n_i}{N} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \quad \dots(5.30)$$

which corresponds to the canonical distribution.

**Example 5.1** A system with just two energy levels is in thermal equilibrium with a heat reservoir at temperature 600 K. The energy gap between the levels is 0.1 eV. Find (i) the probability that the system is in the higher energy level and (ii) the temperature at which this probability will equal 0.25.

$$(i) \quad P = \frac{e^{-\beta E}}{Z} = \frac{e^{-\beta E}}{1 + e^{-\beta E}} = \frac{1}{e^{\beta E} + 1} = \frac{1}{e^{\frac{1.6 \times 10^{-19}}{1.38 \times 10^{-16} \times 600}} + 1} \\ = 0.126$$

$$(ii) \quad \frac{1}{e^{\frac{1.6 \times 10^{-19}}{1.38 \times 10^{-16} \times T}} + 1} = 0.25$$

$$\text{Therefore } T = 1056 \text{ K}$$

**Example 5.2** A solid containing non-interacting paramagnetic atoms, each having a magnetic moment equal to one Bohr magneton, is placed in a magnetic induction field of strength 3 Tesla. Assuming that the atoms are in thermal equilibrium with the lattice, find the temperature to which the solid must be cooled, so that more than 60% of the atoms are polarized with their magnetic moments parallel to the magnetic field.

(One Bohr magneton  $\mu = 9.271 \times 10^{-24} \text{ JT}^{-1}$ )

Here the probability that the molecules are polarized parallel to the field

$$= \frac{e^{\mu B / kT}}{e^{-\mu B / kT} + e^{\mu B / kT}} = \frac{1}{e^{-2\mu B / kT} + 1} = 0.6$$

$$\text{Therefore } e^{-2\mu B / kT} = \frac{0.4}{0.6}$$

$$\text{i.e. } \frac{2\mu B}{kT} = \ln 1.5$$

$$\text{Therefore } T = \frac{2\mu B}{k \ln 1.5} = 9.91 \text{ K}$$

## 5.4 MEAN VALUE AND FLUCTUATIONS

We have seen in Ch. 2, that the mean of a function  $f_\alpha$  is given by

$$\langle f \rangle = \sum_{\alpha} f_{\alpha} P_{\alpha}$$

In the case of canonical distribution

$$\langle f \rangle = \sum_{\alpha} f_{\alpha} \frac{e^{-\beta E_{\alpha}}}{\sum e^{-\beta E_{\alpha}}} \quad \dots(5.31)$$

Thus, mean energy is given by

$$\langle E \rangle = \sum \frac{E_{\alpha} e^{-\beta E_{\alpha}}}{\sum e^{-\beta E_{\alpha}}} = \sum \frac{E_{\alpha} e^{-\beta E_{\alpha}}}{Z}$$

$$\text{Thus, } \langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} (\ln Z) \quad \dots(5.32)$$

The mean square energy is

$$\langle E^2 \rangle = \sum \frac{E_{\alpha}^2 e^{-\beta E_{\alpha}}}{\sum e^{-\beta E_{\alpha}}} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} \quad \dots(5.33)$$

Therefore, fluctuations in energy is

$$\begin{aligned} \langle (\Delta E)^2 \rangle &= \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 \\ &= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 \\ &= \frac{\partial^2}{\partial \beta^2} (\ln Z) = -\frac{\partial \langle E \rangle}{\partial \beta} \end{aligned} \quad \dots(5.34)$$

Using the relation

$$\beta = \frac{1}{kT} \quad \dots(5.35)$$

(to be derived later), we get

$$\langle (\Delta E)^2 \rangle = -\frac{\partial \langle E \rangle}{\partial \beta} = \frac{\partial \langle E \rangle}{\partial T} \frac{\partial T}{\partial \beta} = kT^2 \frac{\partial \langle E \rangle}{\partial T} = kT^2 C_v \quad \dots(5.36)$$

Therefore, the energy fluctuation in the canonical distribution is proportional to the specific heat.

For example, for a perfect gas  $E = \frac{3}{2} NkT$

(This will be proved later)

$$\text{Therefore } \langle (\Delta E)^2 \rangle = kT^2 \frac{3}{2} Nk = \frac{3}{2} Nk^2 T^2 \quad \dots(5.37)$$

and the mean fractional fluctuation

$$\left\{ \frac{\langle (\Delta E)^2 \rangle}{\langle E \rangle^2} \right\}^{\frac{1}{2}} = \left\{ \frac{3Nk^2T^2}{2} \frac{4}{9N^2k^2T^2} \right\}^{\frac{1}{2}} = \left( \frac{2}{3N} \right)^{\frac{1}{2}} \quad \dots(5.38)$$

This is negligible if  $N \gg 1$ .

If  $N = 1$ , fractional fluctuation is  $= \left( \frac{2}{3} \right)^{\frac{1}{2}} = 0.82$ , showing that fluctuations are more important for microscopic systems.

If  $N = 10^{18}$ , say, which corresponds to a macroscopic system, fractional fluctuation is  $0.82 \times 10^{-9}$ , which is negligible. It is, therefore, reasonable to assume that in thermal equilibrium a macroscopic system has a precise energy value, which is equal to the ensemble average value of energy.

## 5.5 GRAND CANONICAL ENSEMBLE

We now consider a situation slightly different from the one considered in the case of canonical distribution. Imagine as before a sub-system  $A$  in a system  $A^1$  with a difference that the walls of the sub-systems are such that  $A$  and  $A^1$  can exchange both energy and particles. Such systems are known as *open systems*.  $A^1$  is, of course, a member of a microcanonical ensemble. If  $E_0, N_0$ , are the energy and number of particles of the entire system

$$\begin{aligned} E_0 &= E_\alpha + E^1 \\ N_0 &= N_\alpha + N^1 \end{aligned} \quad \dots(5.39)$$

where  $E_\alpha, E^1$  and  $N_\alpha, N^1$  are the energies and number of particles in  $A$  and  $A^1$  respectively, and none of them is constant. In deriving the probability distribution, we adopt the same technique as in the case of canonical distribution.

The probability that the sub-system  $A$  is in a state with energy  $E_\alpha$  and number of particles  $N_\alpha$ , is given by

$$P_\alpha = C \Omega_\alpha (E_0 - E_\alpha, N_0 - N_\alpha) \quad \dots(5.40)$$

where  $C$  is a constant and  $\Omega_\alpha$  has the same meaning as in the case of canonical distribution.

We expand  $\ln \Omega_\alpha (E_0 - E_\alpha, N_0 - N_\alpha)$  in a power series

$$\begin{aligned} \ln \Omega_\alpha (E_0 - E_\alpha, N_0 - N_\alpha) &= \ln \Omega_\alpha (E_0, N_0) \\ &\quad - \frac{\partial(\ln \Omega_\alpha)}{\partial E_0} (E_\alpha - \frac{\partial(\ln \Omega_\alpha)}{\partial N_0} N_\alpha) + \dots \\ &= \ln \Omega_\alpha (E_0, N_0) - \beta E_\alpha + \mu N_\alpha \end{aligned} \quad \dots(5.41)$$

where we have put

$$\beta = \frac{\partial(\ln \Omega_\alpha)}{\partial E_0}, \quad -\mu = \frac{\partial(\ln \Omega_\alpha)}{\partial N_0} \quad \dots(5.42)$$

Hence

$$\Omega_\alpha(E_0 - E_\alpha, N_0 - N_\alpha) = \Omega_\alpha(E_0, N_0) e^{-\beta E_\alpha + \mu N_\alpha}$$

$$\text{Therefore } P_\alpha = C e^{-\beta E_\alpha + \mu N_\alpha} \quad \dots(5.43)$$

The normalization condition gives

$$C = \frac{1}{\sum_\alpha e^{-\beta E_\alpha - \mu N_\alpha \beta}} \quad \dots(5.44)$$

and hence

$$P_\alpha = \frac{e^{-\beta E_\alpha - \mu N_\alpha \beta}}{\sum_\alpha e^{-\beta E_\alpha - \mu N_\alpha \beta}} \quad \dots(5.45)$$

This distribution is called the *grand canonical distribution*.

We now introduce here a quantity

$$z = e^{-\beta \mu} \quad \dots(5.46)$$

which is generally known as the *fugacity* of the system. In the chemical literature it is known as the *absolute activity*.

In terms of fugacity the relation (5.45) becomes

$$P_\alpha = \frac{z^{N_\alpha} e^{-\beta E_\alpha}}{\sum_\alpha z^{N_\alpha} e^{-\beta E_\alpha}} \quad \dots(5.47)$$

The denominator in Eq. (5.47) is called the *grand partition function*.

## 5.6 ALTERNATIVE DERIVATION OF THE GRAND CANONICAL DISTRIBUTION

We will now show how we can arrive at the distribution given by Eq. (5.45) by following the techniques adopted in Sec. 5.3 for canonical distribution.

As before, the probability that  $n_1$  systems are in state 1 with energy  $E_1$ ,  $n_2$  in state 2 with energy  $E_2$ , etc. is given by

$$W = \frac{1}{C} \frac{N!}{n_1! n_2! \dots}$$

where  $N$  is the total number of systems in the ensemble. Let  $N_1$  be the number of particles in each of the  $n_1$  systems  $N_2$  in each of the  $n_2$  systems, etc.

Now

$$\ln W = \ln N! - \sum_s \ln n_s! - \ln C$$

$$= N \ln N - N - \sum_s n_s \ln n_s + \sum_s n_s - \ln C$$

The condition for  $\ln W$  to be maximum is

$$\delta \ln W = 0$$

i.e.  $\sum \ln n_s \delta n_s = 0$  ... (5.48)

subject to the conditions

$$\sum_s n_s = N; \frac{\sum n_s \langle E_s \rangle}{N} = \langle E \rangle; \frac{\sum n_s \langle N_s \rangle}{N} = \langle N \rangle$$

$$(i) \sum_s \delta n_s = 0; (ii) \sum_s E_s \delta n_s = 0 \quad (iii) \sum_s N_s \delta n_s = 0.$$

Multiplying (i), (ii) and (iii) by Lagrange's multipliers  $\gamma$ ,  $\beta$  and  $\alpha$  and adding to Eq. (5.48) we get

$$\sum_s (\ln n_s + \gamma + \beta E_s + \alpha N_s) \delta n_s = 0 \quad \dots (5.49)$$

As  $\delta n_s$  are independent their coefficient must vanish

$$\text{Therefore } \ln n_s + \gamma + \beta E_s + \alpha N_s = 0 \quad \dots (5.50)$$

or  $n_s = e^{-\gamma - \beta E_s - \alpha N_s}$  .... (5.51)

Now  $\sum_s n_s = e^{-r} \sum_s e^{\beta E_s - \alpha N_s} = N$

Therefore  $e^{-r} = \frac{N}{\sum_s e^{\beta E_s - \alpha N_s}}$  .... (5.52)

and  $n_s = \frac{N e^{-\beta E_s - \alpha N_s}}{\sum_s e^{\beta E_s - \alpha N_s}}$

The probability of finding the system in state  $s$  is given by

$$P_s = \frac{n_s}{N} = \frac{e^{-\beta E_s - \alpha N_s}}{\sum_s e^{-\beta E_s - \alpha N_s}} \quad \dots (5.53)$$

which is the same as obtained in the preceding section.

## 5.7 FLUCTUATIONS IN THE NUMBER OF PARTICLES OF A SYSTEM IN A GRAND CANONICAL ENSEMBLE

The mean square deviation of the number of particles in an open system is given by

$$\langle (\Delta N)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 \quad \dots (5.54)$$

Now,  $\langle N \rangle = \sum_i P_i N_i = \frac{\sum_i N_i e^{-\beta E_i + \beta \mu N_i}}{Z}$  ... (5.55)

and  $\langle N^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \alpha^2}$  ... (5.56)

We also take  $\alpha = -\beta \mu$ .

But  $\frac{\partial}{\partial \alpha} \left\{ \frac{1}{Z} \frac{\partial Z}{\partial \alpha} \right\} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \alpha^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \alpha} \right)$

Therefore,  $-\frac{\partial \langle N \rangle}{\partial \alpha} = \langle N^2 \rangle - \langle N \rangle^2$

Hence

$$\langle (\Delta N)^2 \rangle = \frac{\partial \langle N \rangle}{\partial \alpha} \quad \dots (5.57)$$

It will be shown in the next chapter  $\alpha = -\beta \mu$ , where  $\mu$  is the chemical potential. Using this relation we can express Eq. (5.57) as

$$\langle (\Delta N)^2 \rangle = kT \frac{\partial \langle N \rangle}{\partial \mu} \quad \dots (5.58)$$

Alternatively, in terms of fugacity  $z$

$$\langle N \rangle = \frac{\sum_i N_i z^{N_i} e^{-\beta E_i}}{Z} = \frac{z}{Z} \frac{\partial Z}{\partial z} = z \frac{\ln Z}{\partial z}$$

Therefore  $z \frac{\partial \langle N \rangle}{\partial z} = \frac{z}{Z^2} \frac{\partial Z}{\partial z} \sum_i N_i z^{N_i} e^{-\beta E_i}$

$$+ \frac{1}{Z} \sum_i N_i^2 z^{N_i} e^{-\beta E_i}$$

$$= -\frac{1}{Z^2} \left[ \sum_i N_i z^{N_i} e^{-\beta E_i} \right]^2 + \frac{1}{Z} \sum_i N_i^2 z^{N_i} e^{-\beta E_i}$$

$$= -\langle N \rangle^2 + \langle N^2 \rangle = \langle (\Delta N)^2 \rangle \quad \dots (5.59)$$

## 5.8 REDUCTION OF GIBBS DISTRIBUTION TO MAXWELL AND BOLTZMANN DISTRIBUTIONS

Since we have claimed that Gibbs distribution is a general distribution, we should be able to derive Maxwell and Boltzmann distributions from it. We now proceed to show how this can be done.

### 5.8.1 Maxwell Distribution

Maxwell distribution function gives basically the probability of finding a particular molecule in a certain range of velocities, say, between  $u$  and

$u + du$ . The system in this case is a single molecule in a heat reservoir. The  $\Gamma$  space is a six-dimensional space, i.e. the M-space.

Since a molecule occupies in the phase space a volume  $h^3$ , the number of states of a molecule contained in a phase volume element  $d\Gamma$  is

$$\frac{d\Gamma}{h^3} = \frac{dx dy dz dp_x dp_y dp_z}{h^6} \quad \dots(5.60)$$

where  $h$  is Planck's constant.

According to Gibbs distribution the probability of a system being in a state with energy  $E_\alpha$  is  $\frac{e^{-\beta E_\alpha}}{\sum e^{-\beta E_\alpha}} g_\alpha$ .

Therefore, the probability of finding the system in a phase volume element  $d\Gamma$  corresponding to the energy  $E_\alpha$  is

$$\begin{aligned} dP_\alpha &= \frac{e^{-\beta E_\alpha}}{\sum e^{-\beta E_\alpha}} \frac{d\Gamma}{h^3} \\ &= \frac{e^{-\beta E_\alpha}}{\sum E^{-\beta E_\alpha}} \frac{dx dy dz dp_x dp_y dp_z}{h^3} \quad \dots(5.61) \end{aligned}$$

To find the probability that the molecule has energy  $E_\alpha$ , we have to integrate Eq. (5.61) with respect to all the elements of the phase volume corresponding to  $E_\alpha$ . Since the energy does not depend upon the coordinates, we can straight away integrate Eq. (5.61) and write

$$dP_\alpha = \frac{V}{h^3} \frac{e^{-\beta E_\alpha}}{\sum e^{-\beta E_\alpha}} dp_x dp_y dp_z \quad \dots(5.62)$$

By converting into spherical coordinates and integrating over all the angular coordinates we have

$$dP_\alpha = \frac{4\pi V}{h^3} \frac{e^{-\beta E_\alpha}}{\sum e^{-\beta E_\alpha}} p^2 dp \quad \dots(5.63)$$

Now  $E = \frac{1}{2} mu^2$ ;  $p = mu$

Substituting these in Eq. (5.63), we have

$$\begin{aligned} dP_\alpha &= \frac{4\pi V}{h^3} \frac{e^{-\beta mu^2/2}}{\sum e^{-\beta mu^2/2}} m^2 u^2 mdu \\ &= \frac{4\pi V m^3}{h^3} \frac{e^{-\beta mu^2/2}}{\sum e^{-\beta mu^2/2}} u^2 du \quad \dots(5.64) \end{aligned}$$

The normalization condition gives  $\int_0^\infty dP_\alpha = 1$ .

That is

$$\frac{4\pi Vm^3}{h^3 \sum e^{-\beta mu^2/2}} \int_0^\infty e^{-\beta mu^2/2} u^2 du = 1$$

i.e.

$$\frac{4\pi Vm^3}{h^3 \sum e^{-\beta mu^2/2}} \frac{1}{2\left(\frac{\beta m}{2}\right)^{\frac{3}{2}}} \Gamma\left(\frac{1}{2}\right)$$

$$= \frac{4\pi Vm^3}{h^3 \sum e^{-\beta mu^2/2}} \frac{\sqrt{2}}{(\beta m)^{\frac{3}{2}}} \frac{\sqrt{\pi}}{2}$$

$$= \frac{4\pi Vm^3}{h^3 \sum e^{-\beta mu^2/2}} \left(\frac{2}{\beta m}\right)^{\frac{3}{2}} \frac{\sqrt{\pi}}{4} = 1$$

Therefore

$$= \frac{4\pi Vm^3}{h^3 \sum e^{-\beta mu^2/2}} = \frac{4}{\sqrt{\pi}} \left(\frac{\beta m}{\sqrt{\pi}}\right)^{\frac{3}{2}} \quad \dots(5.65)$$

Hence

$$dp_\alpha = \frac{4}{\sqrt{\pi}} \left(\frac{\beta m}{2}\right)^{\frac{3}{2}} e^{-\beta mu^2/2} u^2 du \quad \dots(5.66)$$

This is Maxwell distribution. Comparing this with Eq. (3.23), we see that the two relations differ only in the constants appearing in them and will be identical if

$$\beta = 2\alpha m = \frac{2m}{2mkT} = \frac{1}{kT} \quad \dots(5.67)$$

This relation can also be proved by using Eq. (5.67) to calculate mean kinetic energy, as

$$\begin{aligned} \left\langle \frac{mu^2}{2} \right\rangle &= \int_0^\infty \frac{1}{2} mu^2 \frac{4}{\sqrt{\pi}} \left(\frac{\beta m}{2}\right)^{3/2} e^{-\beta mu^2/2} u^2 du \\ &= \frac{2m}{\sqrt{\pi}} \left(\frac{\beta m}{2}\right)^{3/2} \int_0^\infty e^{-\beta mu^2/2} u^4 du \\ &= \frac{2m}{\sqrt{\pi}} \left(\frac{\beta m}{2}\right)^{3/2} \frac{1}{2} \left(\frac{2}{\beta m}\right)^{5/2} \frac{3}{4} \sqrt{\pi} = \frac{3}{2\beta} \end{aligned} \quad \dots(5.68)$$

Using the result proved later

$$\left\langle \frac{1}{2} mu^2 \right\rangle = \frac{3}{2} kT = \frac{3}{2\beta} \quad \dots(5.69)$$

We have

$$\beta = \frac{1}{kT} \quad \dots(5.70)$$

Hence, Maxwell distribution is

$$dP(u) = \frac{4}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{\frac{3}{2}} e^{-\left(\frac{m}{2kT}\right)u^2} u^2 du \quad \dots(5.71)$$

which is the same as Eq. (3.23).

### 5.8.2 Boltzmann Distribution

If the gas is an external potential field, the particle energy  $E_\alpha$  is given by

$$E_\alpha = \frac{1}{2} mu^2 + U(x, y, z) \quad \dots(5.72)$$

where  $U(x, y, z)$  is potential energy of the external field. Therefore

$$dP(x, y, z, p_x, p_y, p_z) = \frac{e^{-\beta\left\{\frac{1}{2}mu^2+U\right\}}}{\sum e^{-\beta\left\{\frac{1}{2}mu^2+U\right\}}} \frac{dx dy dz dp_x dp_y dp_z}{h^3} \quad \dots(5.73)$$

Since the probability densities of coordinates and momenta of a particle are independent

$$dP(x, y, z, px, py, pz) = dP_1(x, y, z) dP_2(p_x, p_y, p_z)$$

where

$$dP_1(x, y, z) = C_1 e^{-\beta U(x, y, z)} dx dy dz \quad \dots(5.74)$$

$$\text{and } dP_2(p_x, p_y, p_z) = C_2 e^{-\beta mu^2/2} dp_x dp_y dp_z \quad \dots(5.75)$$

Here  $C_1, C_2$  are the constants to be found from the normalization condition. The second of these equations was discussed in the preceding section and leads to Maxwell distribution. We will now show that the first leads to Boltzmann distribution.

Equation (5.74) gives the probability that a molecule is located in the volume element  $dxdydz$  at the point  $(x, y, z)$ . If  $N$  is the number of molecules in the system, the number of molecules in the volume element  $dx dy dz$  is

$$dn(x, y, z) = C_1 N e^{-\beta U(x, y, z)} dx dy dz \quad \dots(5.76)$$

Therefore, the concentration at the point  $(x, y, z)$  is .

$$n_0(x, y, z) = \frac{dn}{dx dy dz} = C_1 N e^{-\beta U} \quad \dots(5.77)$$

Suppose, at a given point  $(x_0, y_0, z_0)$  the concentration is  $n_0(x_0, y_0, z_0)$  and potential energy is  $U(x_0, y_0, z_0)$ . Therefore

$$n_0(x_0, y_0, z_0) = C_1 N e^{-\beta U(x_0, y_0, z_0)} \quad \dots(5.78)$$

From Eqs. (5.77) and (5.78) we get

$$\frac{n_0(x, y, z)}{n_0(x_0, y_0, z_0)} = e^{-\beta(U(x, y, z) - (x_0, y_0, z_0))} \quad \dots(5.79)$$

$$\text{i.e. } n_0(x, y, z) = n_0(x_0, y_0, z_0) e^{-\Delta U / kT} \quad \dots(5.80)$$

This is Boltzmann distribution.

**Example 5.3** Calculate the average potential energy of a molecule of an ideal gas in thermal equilibrium at absolute temperature  $T$ , contained in a cubical box of side  $L$ , the only external field acting on the gas being the earth's uniform gravitational field.

Let  $m$  be the mass of a molecule. Hence, its potential energy at height  $z$  from the bottom of the box is  $U = mg z$ . Therefore

$$\begin{aligned}\langle U \rangle &= \frac{\int_0^L mgz e^{-\beta mgz} dz}{\int_0^L e^{-\beta mgz} dz} \\ \text{Numerator} &= mg \left[ \frac{ze^{-\beta mz}}{-mg\beta} - \frac{e^{-\beta mz}}{\beta^2 m^2 g^2} \right]_0^L \\ &= -\frac{Le^{-\beta mgl}}{\beta} + \frac{1}{\beta^2 mg} \\ \text{Denominator} &= \frac{1 - e^{-\beta mgl}}{\beta mg} \\ \langle U \rangle &= -\frac{mgLe^{-\beta mgl}}{1 - e^{\beta mgL}} + \frac{1}{\beta} \\ &= \frac{mgL}{1 - e^{\beta mgL}} + kT\end{aligned}$$

## 5.9 BAROMETRIC FORMULA

As an application of the Boltzmann distribution, we shall now show how it can be used to obtain a formula describing the variation of the atmospheric pressure with altitude. We assume that the atmosphere is in equilibrium and its temperature is constant, which, incidentally, is only an approximate assumption.

If  $m$  is the mass of a molecule and  $h$  is the height at which the concentration is to be found, the potential energy of the molecule at this height

$$\Delta U = mgh \quad \dots(5.81)$$

The concentration at this altitude is

$$n(h) = n(0) e^{-\beta \Delta U} = n(0) e^{-mgh/kT} \quad \dots(5.82)$$

At constant temperature, the pressure is proportional to concentration. Hence, we can write Eq. (5.82) in the form

$$p(h) = p(0) e^{-mgh/kT} \quad \dots(5.83)$$

where  $p(h)$  is the pressure at altitude  $h$  and  $p(0)$  the pressure at  $h = 0$ .

This is known as *Barometric formula*.

## 5.10 EXPERIMENTAL VERIFICATION OF THE BOLTZMANN DISTRIBUTION

Take a vessel with a liquid filled with a powder of very fine particles, whose density is slightly higher than that of the liquid. The particles under the force of gravity will distributed in height non-uniformly in accordance with Eq. (5.82). The ratio of the number of particles at height  $h$  and at the bottom is

$$\frac{n(h)}{n(0)} = e^{-mgh/kT} \quad \dots(5.84)$$

where  $mg$  is the weight of the particle in the liquid. If  $\rho$  is the density of the particle,  $r$  its radius and  $\rho_0$  the density of the liquid

$$mg = \frac{4}{3}\pi r^3 (\rho - \rho_0) g \quad \dots(5.85)$$

where account is taken of the buoyant force acting on the particle.

$$\text{Therefore } \frac{n(h)}{n(0)} = e^{-\frac{4}{3}\pi r^3 (\rho - \rho_0) gh / kT} \quad \dots(5.86)$$

The number of particles at various heights can be measured with the help of a microscope. One can verify whether the concentrations thus measured satisfy Boltzmann distribution.

Experiments of this type were carried out by J Perrin, the results of which confirmed Boltzmann distribution.

The relation (5.86) can be expressed as

$$k = \frac{4/3\pi r^3 (\rho - \rho_0) gh}{T \ln \frac{n(0)}{n(h)}} \quad \dots(5.87)$$

Perrin used this relation to obtain the value of  $k$ .

## 5.11 MIXTURE OF GASES

We have derived Eqs. (5.82) and (5.83) for the variation of concentration and pressure for a single type of particles. We often come across a situation in which two or more types of particles are present. For example, Earth's atmosphere is mainly a mixture of two gases: nitrogen and oxygen. We shall discuss in this section the variation of concentration in the mixture of two gases.

Suppose a cylindrical vessel with base area  $A$  and height  $h$ , contains two types of molecules. Let their total number be  $N_1$  and  $N_2$  and mass of a molecule of each type be  $m_1$  and  $m_2$  respectively. Since the probability that a molecules is located at a particular point is independent of the positions of all other molecules, we can take the distribution of each type

of molecules as

$$\begin{aligned} n_1(h) &= A_1 n_1(0) e^{-m_1 gh / kT} \\ n_2(h) &= A_2 n_2(0) e^{-m_2 gh / kT} \end{aligned} \quad \dots(5.88)$$

where  $n_i(h)$ , are the concentration at height  $h$  and  $A_i$  are constants.

From the normalization condition

$$\begin{aligned} A_1 \int_0^{h_0} n_1(0) e^{m_1 gh / kT} dh &= N_1 \\ i.e. \quad A_1 n_1(0) \left[ -\frac{kT}{m_1 g} e^{m_1 gh / kT} \right]_0^{h_0} &= N_1 \\ \text{or,} \quad A_1 n_1(0) \frac{kT}{m_1 g} \left\{ 1 - e^{m_1 gh_0 / kT} \right\} &= N_1 \end{aligned}$$

$$\text{Therefore} \quad A_1 = \frac{N_1 m_1 g}{n_1(0) k T \left\{ 1 - e^{-m_1 h_0 / kT} \right\}} \quad \dots(5.89)$$

$$\text{and} \quad n_1(h) = \frac{N_1 m_1 g}{k T} \frac{e^{-m_1 gh / kT}}{\left\{ 1 - e^{-m_1 gh_0 / kT} \right\}} \quad \dots(5.90)$$

$$\text{Similarly} \quad n_2(h) = \frac{N_2 m_2 g}{k T} \frac{e^{-m_2 gh / kT}}{\left\{ 1 - e^{-m_2 gh_0 / kT} \right\}} \quad \dots(5.91)$$

These formulae show that the concentration of the heavier molecules decreases rapidly with height.

The ratio of the concentration is

$$\frac{n_2(h)}{n_1(h)} = \frac{N_2 m_2}{N_1 m_1} \cdot \frac{\left\{ 1 - e^{-m_2 gh_0 / kT} \right\}}{\left\{ 1 - e^{-m_1 gh_0 / kT} \right\}} \quad \dots(5.92)$$

**Example 5.4** The Earth's atmosphere at sea level consists of 78% nitrogen and 22% oxygen by volume (The presence of other components is neglected.) Find the percentage content of these gases at an altitude of 8.75 km, assuming the temperature of the atmosphere to be 300K.

The concentrations of the two gases are

$$n_{O_2}(h) = n_{O_2}(0) e^{-m_{O_2} gh / kT}$$

$$n_{N_2}(h) = n_{N_2}(0) e^{-m_{N_2} gh / kT}$$

If  $N$  is the concentration of the mixture at the sea level

$$n_{O_2}(0) = 0.22N; n_{N_2}(0) = 0.78 N$$

The percentage of oxygen content at  $h$  is

$$\begin{aligned}
 &= 100 \frac{0.22 Ne^{-m_{O_2}gh/kT}}{0.22 Ne^{-m_{O_2}gh/kT} + 0.78 Ne^{-m_{N_2}gh/kT}} \\
 &= \frac{0.22}{0.22 + 0.78 e^{-(m_{N_2} - m_{O_2})gh/kT}} \\
 &= 22 \left\{ 1 - \frac{0.78(m_{O_2} - m_{N_2})gh}{kT} \right\}
 \end{aligned}$$

$$m_{O_2} = 5344 \times 10^{-27} \text{ kg}; m_{N_2} = 47.76 \times 10^{-27} \text{ kg}$$

Substituting these values, we get oxygen content in per cent as 19.8%. Hence nitrogen content is 80.2%.

While closing this chapter we have to draw the attention of the reader to the fact that the parameter  $\alpha$  has not yet been identified. This will be done in the next chapter.

## PROBLEMS

- 5.1 Evaluate the partition function at temperature  $T$  for a classical one-dimensional oscillator. Hence find the mean energy of the oscillator.
- 5.2 A small system has just two states of energy  $E_1 = 0$  and  $E_2 = 10^{-22} \text{ J}$ . Find the probabilities  $p_1$  and  $p_2$  for the system to be in states of 1 and 2 respectively, when the mean energy  $\langle E \rangle$  of the system is (i)  $0.2 E_2$ , (ii)  $0.5 E_2$ . Assuming Boltzmann distribution calculate the temperature in the two cases.
- 5.3 A rectangular box of maximum volume is to be made out of a cardboard of fixed area  $A$ . Using the method of Lagrange multipliers, show that the box with maximum volume is a cube.
- 5.4 Show that the specific heat of an ideal gas in the extreme relativistic case is twice its value for unrelativistic monatomic gas.
- 5.5 The number density of magnetic ions in a paramagnetic salt is  $10^{24}/\text{m}^3$ . Each ion has a magnetic moment of one Bohr magneton, which can always be parallel or anti-parallel to the external field. Calculate (i) the difference between the number of ions in these two states, (ii) the mean magnetic energy, if the magnetic field applied is  $1 \text{ T}$  and the temperature  $3 \text{ K}$ .
- 5.6 An infinite column of a classical gas consisting of  $N$  identical atoms each of mass  $m$  is at thermal equilibrium in a uniform gravitational field. Find the mean energy per atom.
- 5.7 A cubical box of side  $L$  contains an ideal gas of  $N$  molecules, each of mass  $m$ , in thermal equilibrium at absolute temperature  $T$ . The only external influence acting on the system is the Earth's

uniform gravitational field. Calculate the average kinetic energy of a molecule.

- 5.8 Assuming that the atmosphere is all at one temperature  $T$ , find the mean height of a gas molecule in the atmosphere.

- 5.9 Find the height at which the atmospheric pressure is  $\frac{1}{100}$  th that of the sea level. Assume that the atmosphere is at a constant temperature 300 K.

- 5.10 Gamboge gum particles were added to a vessel containing water. The density of gum particles is  $1.21 \times 10^3 \text{ kg/m}^3$  and the volume of each grain in  $1.03 \times 10^{-19} \text{ m}^3$ . Find the height at which the concentration of grain distribution decreases to half its value at the bottom of the vessel, the measurements being carried out at 4°C.

- 5.11 Following data on the number of Gamboge particles each of mass  $9.8 \times 10^{-18} \text{ kg}$  and density  $1350 \text{ kg/m}^3$  in water, was obtained in an experiment on gravitational sedimentation equilibrium:

Height in $\mu$	0	25	50	75	100
Mean number of particles	200	175	150	130	110

Calculate the temperature of water.



# SOME APPLICATIONS OF STATISTICAL MECHANICS

In this chapter we will show how the method of statistical mechanics are applied to some physical situations.

## 6.1 ROTATING BODIES

Consider a body rotating with an angular velocity about a fixed axis. Let us find the canonical distribution in the rotating system of coordinates.

Let  $\mathbf{v}$  = velocity of the constituent particles relative to a fixed coordinate system.

$\mathbf{v}'$  = velocity of the particles relative to the coordinate system rotating with the body.

$E$  = energy of the body relative to the fixed coordinate system.

$E'$  = energy of the body relative to the coordinate system rotating with the body.

If  $\mathbf{r}$  is the position vector

$$\mathbf{v} = \mathbf{v}' + \omega \times \mathbf{r} \quad \dots(6.1)$$

where  $\omega$  is the angular velocity vector.

Lagrangian for the body is

$$\begin{aligned} L &= \frac{1}{2} \sum m \mathbf{v}^2 - U, \text{ where } U \text{ is the potential energy} \\ &= \frac{1}{2} \sum m (\mathbf{v}' + \omega \times \mathbf{r})^2 - U \\ &= \frac{1}{2} \sum m \mathbf{v}'^2 + \sum m \mathbf{v}' (\omega \times \mathbf{r}) + \frac{1}{2} \sum m (\omega \times \mathbf{r}')^2 - U \end{aligned} \quad \dots(6.2)$$

Linear momentum  $\mathbf{p}'$ , relative to the coordinate system rotating with the body is given by

$$\begin{aligned} \mathbf{p}' &= \frac{\partial L}{\partial \mathbf{v}'} = \sum m \mathbf{v}' + \sum m (\omega \times \mathbf{r}) \\ &= \sum m (\mathbf{v}' + \omega \times \mathbf{r}) = \sum m \mathbf{v} = \mathbf{p} \end{aligned} \quad \dots(6.3)$$

where  $\mathbf{p}$  is the linear momentum relative to the fixed coordinate system.

We know from mechanics that

$$E' = \sum p'v' - L = \sum \mathbf{p} \cdot \mathbf{v}' - L \quad \dots(6.4)$$

Substituting from Eqs. (6.1) and (6.2)

$$E' = \frac{1}{2} \sum m v'^2 - \frac{1}{2} \sum m (\omega \times \mathbf{r})^2 + U \quad \dots(6.5)$$

Hence, the density distribution for a canonical system is

$$\begin{aligned} \rho_E &= Ce^{-\beta E'} = Ce^{-\beta \left\{ \frac{1}{2} \sum m v'^2 - \frac{1}{2} \sum m (\omega \times \mathbf{r})^2 + U \right\}} \\ &= Ce^{-\beta \left\{ \frac{p_1^2}{2m} + U - \frac{1}{2} \sum m (\omega \times \mathbf{r})^2 \right\}} \end{aligned} \quad \dots(6.6)$$

Therefore

$$\rho_E = Ce^{-\beta \left\{ E - \sum \frac{m(\omega \times \mathbf{r})^2}{2} \right\}} \quad \left( \text{because } p_1^2 = p \text{ and } E = \frac{p^2}{2m} + U \right) \quad \dots(6.7)$$

Thus, the difference between the distribution function of rotating bodies and that of the stationary bodies is the appearance of the additional term

$-\frac{m(\omega \times \mathbf{r})^2}{2}$  in the Boltzmann factor of the former function. This indicates that the rotation is equivalent to the appearance of an external field corresponding to the centrifugal forces.

**Example 6.1** A cylinder of height  $l$  and radius  $R$  is filled with a gas consisting of  $N$  molecules each of mass  $m$ . The cylinder rotates with an angular velocity  $\omega$  about an axis perpendicular to the base and passing through its centre. Determine the density of the gas.

The term to be added to the energy in this case is obviously  $-\frac{1}{2} m \omega^2 r^2$  if  $r$  is the distance of the molecule from the axis.

The density, i.e. the number of molecules per unit volume  $n(r)$ , is therefore

$$n(r) = Ae^{\frac{1}{2}\beta m \omega^2 r^2} \quad \dots(6.8)$$

where  $A$  is a constant.

The number of molecules in a small volume element  $dV = 2\pi r l dr$  is equal to

$$Ae^{\frac{1}{2}\beta m \omega^2 r^2} 2\pi r l dr$$

Since  $N$  is the total number of molecules

$$N = A \int_0^R e^{\frac{1}{2}\beta m \omega^2 r^2} 2\pi r l dr$$

$$= A \int_0^R e^{\frac{1}{2} \beta m \omega^2 r^2} 2\pi r dr$$

Putting

$$x = \frac{\beta m \omega^2 r^2}{2}$$

$$\begin{aligned} N &= \frac{A \cdot 2\pi l}{\beta m \omega^2} \int_0^{\beta m \omega^2 R^2 / 2} e^x dx \\ &= \frac{2\pi Al}{\beta m \omega^2} (e^{\beta m \omega^2 R^2 / 2} - 1) \end{aligned}$$

Therefore

$$A = \frac{N \beta m \omega^2}{2\pi l (e^{\beta m \omega^2 R^2 / 2} - 1)} \quad \dots(6.9)$$

and

$$n(R) = \frac{N \beta m \omega^2}{2\pi l (e^{\beta m \omega^2 R^2 / 2} - 1)} e^{\beta m \omega^2 R^2 / 2} \quad \dots(6.10)$$

## 6.2 THE PROBABILITY DISTRIBUTION FOR ANGULAR MOMENTA AND ANGULAR VELOCITIES OF ROTATION OF MOLECULES

Let  $\omega_1, \omega_2, \omega_3$  be the components of the angular velocity along the principle axes of a molecule and  $I_1, I_2, I_3$  be its principle moments of inertia.

The components of angular momentum, therefore, are

$$M_1 = I_1 \omega_1, M_2 = I_2 \omega_2, M_3 = I_3 \omega_3$$

and the kinetic energy of rotation (regarding the molecule at a single body) is

$$\begin{aligned} \varepsilon_{rd} &= \frac{1}{2} (I_1 \omega_1^2 + I_2 \omega_2^2 + I_3 \omega_3^2) \\ &= \frac{1}{2} \left( \frac{M_1^2}{I_1} + \frac{M_2^2}{I_2} + \frac{M_3^2}{I_3} \right) \quad \dots(6.11) \end{aligned}$$

The probability distribution for the angular momentum is

$$dW_M = Ae^{-\frac{\beta}{2} \left( \frac{M_1^2}{I_1} + \frac{M_2^2}{I_2} + \frac{M_3^2}{I_3} \right)} dM_1 dM_2 dM_3 \quad \dots(6.12)$$

The condition of normalization gives

$$A \int e^{-\frac{\beta}{2} \left( \frac{M_1^2}{I_1} + \frac{M_2^2}{I_2} + \frac{M_3^2}{I_3} \right)} dM_1 dM_2 dM_3 = 1$$

$$\text{Therefore } A \left[ \int_{-\infty}^{\infty} e^{-\frac{\beta M_1^2}{2 I_1}} dM_1 \right] \left[ \int_{-\infty}^{\infty} e^{-\frac{\beta M_2^2}{2 I_2}} dM_2 \right] \left[ \int_{-\infty}^{\infty} e^{-\frac{\beta M_3^2}{2 I_3}} dM_3 \right] = 1$$

$$\text{i.e., } \sqrt{\frac{2\pi I_1}{\beta}} \sqrt{\frac{2\pi I_2}{\beta}} \sqrt{\frac{2\pi I_3}{\beta}} = 1$$

$$\text{or } A = (2\pi kT)^{-3/2} I_1^{-1/2} I_2^{-1/2} I_3^{-1/2} \quad \dots(6.13)$$

and, hence

$$dW_M = (2\pi kT)^{-3/2} (I_1 I_2 I_3)^{-1/2} e^{-\frac{1}{2kT}\left(\frac{M_1^2}{I_1} + \frac{M_2^2}{I_2} + \frac{M_3^2}{I_3}\right)} dM_1 dM_2 dM_3 \quad \dots(6.14)$$

and the probability distribution for angular velocity

$$dW_\infty = (2\pi kT)^{-3/2} (I_1 I_2 I_3)^{-1/2} e^{-\frac{1}{2kT}(I_1 \omega_1^2 + I_2 \omega_2^2 + I_3 \omega_3^2)} d\omega_1 d\omega_2 d\omega_3 \quad \dots(6.15)$$

## 6.3 THERMODYNAMICS

Thermodynamics aims at studying phenomenologically the properties of material bodies characterized by macroscopic parameters. We know that matter in the aggregate can exist in states which are stable and do not change in time. The mechanical properties characterizing these equilibrium states, however, change with temperature.

### 6.3.1 Reversible and Irreversible Process

It is possible for a system to change from one equilibrium state to another. These transitions can take place in two different ways:

- (i) **Infinitely slowly:** After an infinitely small change in parameters, the next change is not made until all macroscopic parameters attain constant values, i.e. the system attains an equilibrium state. A system is said to be in equilibrium when the statistical distributions of the observables averaged over their fluctuations are constant. After this, the next change is made, adopting the same procedure. The entire process, thus, consists of a sequence of equilibrium states and is called *quasistatic equilibrium process*.
- (ii) **Abruptly:** The changes are bought about so abruptly, that the parameters may not assume constant values over the entire system. For example, if we suddenly change the volume of a gas, the pressure and temperature will not be constant over the entire volume and it will be meaningless to characterize the system in terms of pressure and temperature. These are known as *non-equilibrium processes*.

The transition of a system from one state to another can be brought about either (a) reversibly or (b) irreversibly.

In a reversible change, the system remains throughout infinitesimally close to the thermodynamic equilibrium; i.e. the change is carried out

quasi-statically. Such changes are always reversible and the system can be brought back to the original thermodynamic state by reversing the process. In an irreversible change the system cannot be brought to the original state without causing a change in the surroundings.

### 6.3.2 The Laws of Thermodynamics

Phenomenological thermodynamics is based on certain laws. These laws are merely reasonable hypotheses formulated as a result of practical experience. They have been applied to a large number of phenomena and have been proved to be correct. They have, for example, been applied to matter in extreme physical conditions, such as matter in bulk at nuclear densities inside neutron stars in the early stages of the hot Big Bang Model of the universe:

- (i) **Zeroth law of thermodynamics.** The law states that *if two systems A and B are in thermal equilibrium with a third system C, then A and B must also be in thermal equilibrium with each other.* This law forms the basis of thermometry.
- (ii) **First law of thermodynamics.** This is the law of conservation of energy. A system containing a large number of particles will always have in its equilibrium state an internal energy  $U$  due to the movements of the particles constituting the system and their interactions. If an amount of heat  $\delta Q$  is supplied to the system, the change in the energy is given by

$$\delta Q = dU + \delta W \quad \dots(6.16)$$

where  $\delta W$  is the work done by the system. By convention, the work done by the system is taken to be positive, while the work done on the system is taken to be negative.

Suppose a gas is contained in a cylindrical vessel with a piston (Fig. 6.1) of cross-section  $A$ . The force acting on the piston due to the mean pressure  $\langle p \rangle$  is  $\langle p \rangle A$ . The work done by displacing the piston through a distance  $dx$  is

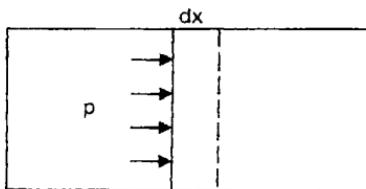


Fig. 6.1

$\langle p \rangle A dx = \langle p \rangle dV$ . Hence, we can write Eq. (6.16) as

$$\delta Q = dU + \langle p \rangle dV \quad \dots(6.17)$$

The relation (6.16) is the mathematical expression for the first law of thermodynamics.

Note that we have used the symbols  $\delta Q$ ,  $\delta W$  for the heat absorbed and the work done, while  $dU$  for the change in internal energy. This distinction between the differentials is to show which of them refer to the function of the state and which do not.  $dU$  is an exact differential of the function of the state. In the same way  $dp$ ,  $dV$ ,  $dT$  are also exact differentials. But  $\delta Q$ ,  $\delta W$  are not, because you can always bring out the same change  $dV$  in the system by adjusting  $\delta Q$ ,  $\delta W$ .

- (iii) **Second law of thermodynamics.** This law is expressed in several ways, one of them being:

'No process is possible whose sole aim is the transfer of heat from a colder to a hotter body'.

There is yet another way in which this law can be expressed. From the first law we have

$$\delta Q = dU + pdV$$

Dividing both sides by  $T$

$$\frac{\delta Q}{T} = \frac{dU}{T} + \frac{p}{T} dV \quad \dots(6.18)$$

The specific heat  $C_V$  is a function of the state and is given by

$$C_V = \frac{dU}{dT} \text{ or } dU = C_V dT$$

From the equation of state of gas

$$pV = RT \quad \text{i.e.} \quad p = \frac{RT}{V}$$

where  $R$  is the gas constant.

Using these relations Eq. (6.18) can be written as

$$\frac{\delta Q}{T} = C_V \frac{dT}{T} + R \frac{dV}{V} = d(C_V \ln T + R \ln V) \quad \dots(6.19)$$

Since the right-hand side is an exact differential, the left-hand side must also be an exact differential. The function of the state whose differential is  $\frac{\delta Q}{T}$  is called the *entropy* of the system and is denoted by  $S$ . Thus

$$dS = \frac{\delta Q}{T} \quad \dots(6.20)$$

This is a quantity of which we have no intuitive knowledge. Note that this relation enables us to measure the change in entropy caused by a transition from one equilibrium state to another. It does not give the value of entropy in each state.

The second law of thermodynamics states that *when a system goes from one state to another by absorbing heat slowly, quasi-statistically at constant temperature its entropy increases*.

- (iv) **Third law of thermodynamics.** *The entropy  $S$  has a limiting value  $S_0$  as the temperature tends to zero.*

$S_0$  is independent of nature of the system and its numerical value is not fixed at 0 K, but it is convenient to take it to be equal to zero. The third law of thermodynamics is also known as the Nernst heat theorem and is best developed and interpreted using statistical mechanics.

## 6.4 STATISTICAL INTERPRETATION OF THE BASIC THERMODYNAMIC VARIABLES

We will now take up the discussion of the basic thermodynamic variables; pressure  $P$ , entropy  $S$ , etc., and show how statistical analysis results in relatively simple and explicit relationships for all these quantities which ultimately lead to thermodynamic laws.

### 6.4.1 Energy and Work

The energy of a system usually depends not only upon the generalized coordinates and momenta, but also upon the parameters such as the volume of the system, or the applied magnetic or electric field, etc., which are known to affect the equation of motion of the system. These parameters are termed as *external parameters* of the system.

Suppose, the system is acted upon by an external parameter  $X$ . A change  $dx$  in this parameter, will cause a change  $dE_s$  in the energy of the system in the state  $s$ , given by

$$dE_s = \frac{\partial E_s}{\partial x} dx \quad \dots(6.21)$$

The mean work done by the system as a result of such changes is

$$\begin{aligned} \langle dW \rangle &= \sum_s P(E_s) dE_s = \frac{\sum e^{-\beta E_s} (-\partial E_s)}{\sum e^{-\beta E_s}} \\ &= \frac{\sum e^{-\beta E_s} \left( -\frac{\partial E_s}{\partial x} \right) dx}{\sum e^{-\beta E_s}} = \frac{1}{Z} \frac{1}{\beta} \frac{\partial}{\partial x} \left( \sum e^{-\beta E_s} \right) dx \\ &= \frac{1}{Z} \frac{1}{\beta} \frac{\partial Z}{\partial x} dx = \frac{1}{\beta} \frac{\partial (\ln Z)}{\partial x} dx \\ &= kT \frac{\partial}{\partial x} (\ln Z) dx \quad \dots(6.22) \end{aligned}$$

where we have assumed canonical distribution. Thus, knowing the partition function and the temperature, we can find the work done by the system.

### 6.4.2 Pressure

In the case of an ideal gas, in order to reduce the volume occupied by the gas, a certain amount of work must be done on the gas to overcome the forces of pressure. The work done by displacing the piston (Fig. 6.1) through  $dx$  is

$$\langle dW \rangle = \langle p \rangle Adx = \langle p \rangle dV \quad \dots(6.23)$$

In this case the external parameter is  $V$ . Replacing  $x$  by  $V$  in Eq. (6.22) the mean work done is

$$\langle dW \rangle = \frac{1}{\beta} \frac{\partial(\ln Z)}{\partial V} dV \quad \dots(6.24)$$

Comparing Eqs. (6.23) and (6.24), we get

$$\langle p \rangle = \frac{1}{\beta} \frac{\partial(\ln Z)}{\partial V} = kT \frac{\partial(\ln Z)}{\partial V} \quad \dots(6.25)$$

### 6.4.3 Entropy

Entropy is one of the most important physical quantities in thermodynamics. The thermodynamics definition of entropy, however does not enable us to understand why this state function plays such a major role in thermodynamics. Its statistical interpretation is much more specific.

The partition function  $Z$  is a function of  $\beta$  and  $E_s$ . Energy  $E_s$ , in its turn is a function of external parameter  $x$ .

$$\begin{aligned} \text{Therefore } d(\ln Z) &= \frac{\partial(\ln Z)}{\partial \beta} d\beta + \frac{\partial(\ln Z)}{\partial x} dx \\ &= -\langle E \rangle d\beta + \beta \langle dW \rangle \end{aligned}$$

when we have used Eqs. (5.30) and (6.22),

$$\text{or } d(\ln Z) = d - d(\beta \langle E \rangle) + \beta d \langle E \rangle + \beta \langle dW \rangle$$

$$\text{Therefore } d(\ln Z + \beta \langle E \rangle) = \beta(d \langle E \rangle + \langle dW \rangle) \quad \dots(6.26)$$

Now

$$\delta Q = d \langle E \rangle + \langle dW \rangle$$

$$\text{Therefore, } (\ln Z + \beta \langle E \rangle) = \beta \delta Q$$

$$dk(\ln Z + \beta \langle E \rangle) = \frac{\delta Q}{T} = dS \quad \dots(6.27)$$

$$\text{Therefore } S = k(\ln Z + \beta \langle E \rangle) \quad \dots(6.28)$$

This is the expression for the entropy  $S$  in terms of the partition function  $Z$  and the mean energy  $\langle E \rangle$ .

Entropy  $S$  can also be expressed in other forms.

We know that the most probable state is more probable than any other state. The only contribution which is important in  $Z$ , therefore, is that due to the most probable energy, which in turn is the mean energy. Hence, we can write for  $Z$  an approximation.

$$Z = e^{-\beta \langle E \rangle} \Omega(\langle E \rangle) \quad \dots(6.29)$$

where  $\Omega(\langle E \rangle)$  is the number of states with mean energy  $\langle E \rangle$ . Using this in Eq. (6.28)

$$\begin{aligned} S &= k \{ -\beta \langle E \rangle + \ln \Omega(\langle E \rangle) + \beta \langle E \rangle \} \\ &= k \ln \Omega(\langle E \rangle) \end{aligned} \quad \dots(6.30)$$

Thus the entropy  $S$  of a system is determined by the logarithm of the number of microstates, through which a given macrostate is realized.

Although Eq. (6.30) has been derived for an ideal gas, it is valid for all systems. It also provides a clear interpretation of entropy. The more ordered a system lower is the number of microstates through which a macrostate is realized and, hence, lower is its entropy. That is, if all the particles in a system are fixed at definite positions, there is only one accessible microstate and its entropy, as given by Eq. (6.30) is zero since  $\Omega(\langle E \rangle) = 1$ . With the increasing number of microstates the entropy increases. It also must be noted that with the increasing number of accessible microstates, the system becomes more and more disordered. The entropy of a system, therefore, is a measure of its disorder or of the chaotic state of the system.

The equilibrium state of a system is the most probable state corresponding to a given condition and is attained through the largest number of microscopic states. The entropy of the system, therefore, attains its maximum value in this state. A system always tends to move towards the equilibrium state; that is, *in the direction in which entropy increases*. This can as well be taken as the statement of the second law of thermodynamics.

It must be mentioned here that the definition of entropy in terms of the partition function  $Z$  and the mean energy  $\langle E \rangle$ , is more convenient than the one given in Eq. (6.30). Since  $Z$  involves an unrestricted sum over all states, its computation is relatively simpler than counting the states  $\Omega(E)$  within the range between  $E$  and  $E + dE$ .

**Example 6.2** Show that if one erg of heat is added to a mole of copper which is initially at absolute zero, the temperature of the copper rises to 0.0169 K and the increase in the entropy is  $1.18 \times 10^{-5}$  J K<sup>-1</sup>. Find also the number of microstates accessible to the copper. The molar heat capacity of coppers is  $7 \times 10^{-4}$  TJ K<sup>-1</sup>, where T is the absolute temperature and volume of the copper is kept constant.

$$(1) \quad \delta Q = \frac{dU}{dT} dT = 7 \times 10^{-4} T dT$$

$$\text{Therefore } \int \delta Q = 7 \times 10^{-4} \frac{T^2}{2} = 10^{-7}$$

$$\text{or } T = \left( \frac{2 \times 10^{-7}}{7 \times 10^{-4}} \right)^{1/2} = 0.0169 \text{ K}$$

$$(2) \quad dS = \int C_V d(\ln T) = \int 7 \times 10^{-4} dT \\ = 7 \times 10^{-4} \times 0.0169 = 1.18 \times 10^{-5} \text{ JK}^{-1}$$

$$(3) \quad S = k \ln \Omega$$

$$\text{Therefore } \ln \Omega = \frac{S}{k} = \frac{1.18 \times 10^{-5}}{1.38 \times 10^{-23}} = 0.855 \times 10^{18} \\ \Omega = e^{(8.55 \times 10^{17})}$$

#### 6.4.4 Change in Entropy with the Change in Volume

In the light of arguments given above, one can easily understand why the entropy increases with increasing volume. With increasing volume, the number of positions available for a fixed number of particles increases. Thus, more distributions or more accessible states are possible and, hence, entropy increases as can be seen from Eq. (6.30).

Mathematically, this can be shown as follows:

From Eq. (6.19) we see that, in an isothermal process (*i.e.*  $T = \text{constant}$ ) any change in entropy is due to the change in volume  $V$ .

$$dS = \frac{\delta Q}{T} = d(C_V \ln T + R \ln V) \\ = R d(\ln V) \quad \dots(6.31)$$

when  $T$  is constant.

If the volume changes from  $V_1$  to  $V_2$

$$\int_{V_1}^{V_2} dS = R \int_{V_1}^{V_2} d(\ln V)$$

$$\text{i.e. } S_2 - S_1 = R (\ln V_2 - \ln V_1) = R \ln \frac{V_2}{V_1} \quad \dots(6.32)$$

**Example 6.3** Show how the work done by an ideal gas during isothermal expansion can be expressed in terms of the change in entropy.

$$W = \int_{V_1}^{V_2} p dV = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ln \frac{V_2}{V_1} \\ = T(S_2 - S_1) \quad \dots(6.33)$$

#### 6.4.5 Change in Entropy with the Change in Temperature

If the volume is constant, *i.e.*  $dV = 0$  (isochoric process), we have from Eq. (6.19)

$$S_2 - S_1 = \Delta S = \int_1^2 C_V d(\ln T) = C_V \ln \frac{T_2}{T_1} \quad \dots(6.34)$$

This relation shows that the entropy increases with temperature as one should expect. With the increase in temperature mean energy increases, resulting in an increase in the number of energy states.

**Example 6.4** Two vessels of volume  $V_1$  and  $V_2$  contain molecules of the same gas at temperatures  $T_1$  and  $T_2$ , respectively, their pressures being the same. The two vessels are then connected with each other. The gases mix with each other and attain a state of equilibrium. Find the change in entropy during the process.

The final temperature and volume of the mixture are  $\frac{T_1 + T_2}{2}$  and  $V_1 + V_2$ , respectively. The changes in the entropy of the two gases are

$$\begin{aligned}\Delta S_1 &= \left\{ C_V \ln \frac{T_1 + T_2}{2} + R \ln(V_1 + V_2) \right\} - (C_V \ln T_1 + R \ln V_1) \\ &= C_V \ln \frac{T_1 + T_2}{2T_1} + R \ln \frac{V_1 + V_2}{V_1} \\ \Delta S_2 &= C_V \ln \frac{T_1 + T_2}{2T_2} + R \ln \frac{V_1 + V_2}{V_2}\end{aligned}$$

Therefore

$$\begin{aligned}\Delta S &= \Delta S_1 + \Delta S_2 = C_V \ln \frac{(T_1 + T_2)^2}{4T_1 T_2} + R \ln \frac{(V_1 + V_2)^2}{V_1 V_2} \\ &= C_V \ln \frac{(T_1 + T_2)^2}{4T_1 T_2} + R \ln \frac{R^2 (T_1 + T_2)^2 / 4p^2}{R^2 T_1 T_2 / p^2} \\ &= C_V \ln \frac{(T_1 + T_2)^2}{4T_1 T_2} + R \ln \frac{(T_1 + T_2)^2}{4T_1 T_2} \\ &= C_V \ln \frac{(T_1 + T_2)^2}{4T_1 T_2} + (C_p - C_V) \ln \frac{(T_1 + T_2)^2}{4T_1 T_2} \\ &= C_p \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}\end{aligned}$$

#### 6.4.6 Entropy for Adiabatic Processes

From Eq. (6.19) we obtain

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \dots(6.35)$$

For adiabatic processes we have

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \gamma = \frac{C_p}{C_V}; C_p - C_V = R \quad \dots(6.36)$$

$$\text{Therefore } \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \text{ and } \ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_2}{V_1}$$

Hence

$$\begin{aligned} S_2 - S_1 &= C_v(\gamma - 1) \ln \left( \frac{V_1}{V_2} \right) + (C_p - C_v) \ln \frac{V_2}{V_1} \\ &= (C_p - C_v) \left\{ -\ln \frac{V_2}{V_1} + \ln \frac{V_2}{V_1} \right\} = 0 \end{aligned} \quad \dots(6.37)$$

Thus, in an adiabatic process, the entropy does not change. This can be easily understood. In an adiabatic expansion, the entropy increases because the volume increases. But with the expansion, temperature decreases. Therefore the entropy decreases. The two tendencies completely compensate each other.

#### 6.4.7 Entropy in Terms of Probability

We know that the probability that a system is in a state  $s$ , with energy  $E_s$  is given by

$$P_s = \frac{e^{-\beta E_s}}{Z}$$

$$\text{Therefore } E_s = -\frac{1}{\beta} \ln (Z, P_s)$$

$$\text{Now } \langle E \rangle = \sum_s P_s E_s$$

$$\begin{aligned} \text{i.e. } \langle E \rangle &= \beta \sum_s P_s E_s = - \sum_s P_s \ln (Z P_s) \\ &= - \sum_s P_s \ln Z - \sum_s P_s \ln P_s \\ &= \ln Z - \sum_s P_s \ln P_s \quad (\text{because } \sum_s P_s = 1) \end{aligned}$$

Therefore

$$\begin{aligned} S &= k (\ln Z + \beta \langle E \rangle) \\ &= -k \sum_s P_s \ln P_s \end{aligned} \quad \dots(6.38)$$

This shows that the entropy is connected with the fact that a system is not in a definite state, but is spread over a large number of states according to some probability distribution.

This relation leads to an interesting conclusion which, in turn, shows that the relation is consistent with the Nernst heat theorem or the Third law of thermodynamics. At  $T = 0$  K, the system will be in its ground state. If this state is unique the system will be found in this state with certainty, i.e.  $P_s = 1$  and, therefore,  $S$  will be equal to zero which is essentially the content of the third law.

### 6.4.8 Additive Property of Entropy

The additive property of entropy can easily be illustrated when it is expressed in the form of Eq. (6.38).

Imagine a composite system  $A^0$  consisting of the two systems  $A$  and  $A^1$ . Suppose that the probability of finding  $A$  in a state  $r$  is  $P_r^{(1)}$  and that of finding  $A^1$  in a state  $s$  is  $P_s^{(2)}$ . Their respective entropies, therefore, will be

$$S_1 = -k \sum P_r^{(1)} \ln P_r^{(1)} \text{ and } S_2 = -k \sum P_s^{(2)} \ln P_s^{(2)}$$

Let us represent the probability of finding the composite system  $A^0$  in the state in which  $A$  is in  $r$  state and  $A^1$  in  $s$  state, by the symbol  $P_{rs}$ . If  $A$  and  $A^1$  are weakly interacting,  $P_{rs} = P_r^{(1)} P_s^{(2)}$ .

Now the entropy of the composite system using relation (6.39) will be

$$\begin{aligned} S &= -k \sum_r \sum_s P_{rs} \ln P_{rs} \\ &= -k \sum_r \sum_s P_r^{(1)} P_s^{(2)} \ln (P_r^{(1)} P_s^{(2)}) \\ &= -k \sum_r \sum_s P_r^{(1)} P_s^{(2)} (\ln P_r^{(1)} + \ln P_s^{(2)}) \\ &= -k \sum_s P_s^{(2)} \sum_r P_r^{(1)} \ln P_r^{(1)} - k \sum_r P_r^{(1)} \sum_s P_s^{(2)} \ln P_s^{(2)} \\ &= -k \sum_r P_r^{(1)} \ln P_r^{(1)} - k \sum_s P_s^{(2)} \ln P_s^{(2)} \\ &\quad \left( \text{because } \sum_r P_r^{(1)} = \sum_s P_s^{(2)} = 1 \right) \\ &= S_1 + S_2 \end{aligned} \quad \dots(6.39)$$

The relation (6.38) is sometimes taken as the starting point in the treatment of statistical problems, particularly in the study of information theory.

### 6.4.9 Helmholtz Free Energy

It is possible to store energy in a thermodynamic system by doing work on it through a reversible process and eventually it can be retrieved in the form of work. The energy which can be stored and is retrievable is called *free energy*. There are different forms of free energy in a thermodynamic system, e.g. (i) internal energy  $U$  (ii) Helmholtz free energy  $F$ ; (iii) Gibbs free energy  $G$  and (iv) enthalpy  $H$ .

From the first law of thermodynamics we have

$$\delta Q = d\langle U \rangle + \delta W$$

or

$$\delta W = pdV = -d\langle U \rangle + \delta Q = -d\langle U \rangle + TdS \quad \dots(6.40)$$

In an isothermal process  $T$  is constant

$$\text{Therefore } \delta W = -d(\langle U \rangle - TS) = -dF$$

The quantity

$$F = \langle U \rangle - TS \quad \dots(6.41)$$

is known as *Helmholtz free energy*. In isothermal processes it plays the role of potential energy. Its variation with the opposite sign is equal to the work performed.

We can express Helmholtz free energy in terms of partition function:

$$\begin{aligned} F &= \langle U \rangle - TS = \langle U \rangle - Tk (\ln Z + \beta \langle U \rangle) \\ &= -kT \ln Z \end{aligned} \quad \dots(6.42)$$

In the same manner, using the results obtained so far we can express the other thermodynamics functions, also known as *thermodynamic potentials*, in terms of  $Z$ . These are

$$\text{Enthalpy } H = U + pV \quad \dots(6.43)$$

$$\text{and Gibbs free energy } G = U - TS + pV \quad \dots(6.44)$$

## 6.5 PHYSICAL INTERPRETATION OF $\alpha$

We have already identified  $\beta$  with temperature. How do we interpret  $\alpha$ ?

If  $\delta Q$  is the heat absorbed by a system and  $\delta W$  is the work done by it, the resulting increase in the energy of the system is given by

$$dU = \delta Q - \delta W \quad \dots(6.45)$$

If the only work done is that due to a change in volume,

$$dU = \delta Q - pdV = TdS - pdV \quad \dots(6.46)$$

However, when the number of particles in the system is not constant, we have also to take into account the change in energy contributed when the particles are added to the system.

Let  $\mu$  be the change in energy of the system when a single particle is added to it.  $\mu$  is called the *chemical potential of the system*.

$$dU = TdS - pdV + \mu dN \quad \dots(6.47)$$

where  $dN$  is the change in the number of particles. If the system contains more than one type of particles, Eq. (6.47) takes the form

$$dU = TdS - pdV + \sum \mu_i \delta N_i \quad \dots(6.48)$$

From Eq. (6.47), we get

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN \quad \dots(6.49)$$

$$\text{Therefore, } \left( \frac{\partial S}{\partial U} \right)_{V, N} = \frac{1}{T}; \left( \frac{\partial S}{\partial V} \right)_{U, N} = \frac{P}{T}; \left( \frac{\partial S}{\partial N} \right)_{U, V} = -\frac{\mu}{T} \quad \dots(6.50)$$

On the other hand, since

$$S = k \ln \Omega(U, N) \quad \dots(6.51)$$

$$dS = k \left\{ \frac{\partial \ln \Omega}{\partial U} dU + \frac{\partial \ln \Omega}{\partial N} dN \right\} \quad \dots(6.52)$$

$$\text{Therefore } \left( \frac{\partial S}{\partial U} \right)_{V,N} = k \frac{\partial \ln \Omega}{\partial U} = k\beta = \frac{1}{T} \quad \dots(6.53)$$

and

$$\left( \frac{\partial S}{\partial U} \right)_{U,V} = k \frac{\partial \ln \Omega}{\partial N} = k\alpha = \frac{\mu}{T} \quad \dots(6.54)$$

$$\text{Therefore } \alpha = -\frac{\mu}{kT} = -\beta\mu \quad \dots(6.55)$$

Thus,  $\alpha$  is related to the chemical potential by the relation (6.55). Fugacity, therefore, is given by

$$z = e^{-\alpha} = e^{\mu/kT} \quad \dots(6.56)$$

## 6.6 CHEMICAL POTENTIAL IN THE EQUILIBRIUM STATE

Consider two systems  $A$  and  $A^1$  with particles  $N_1$  and  $N_2$  and chemical potentials  $\mu_1$  and  $\mu_2$  respectively. Suppose that the temperature and pressure of the systems are the same and that they are in contact, being separated by a permeable partition (Fig. 6.2).

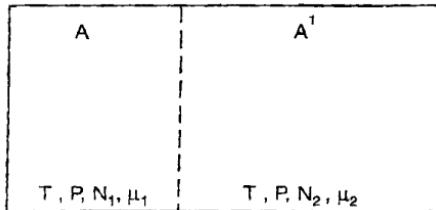


Fig. 6.2

The free energy is given by

$$F = U - TS$$

Therefore

$$dF = dU - TdS - S dT \quad \dots(6.57)$$

Equation (6.48) gives

$$dU = TdS - pdV + \sum_i \mu_i dN_i$$

$$\text{Therefore, } dF = -SdT - pdV + \sum_i \mu_i dN_i \quad \dots(6.58)$$

If  $T$  and  $V$  are maintained constant

$$dF = \sum_i \mu_i dN_i \quad \dots(6.59)$$

Therefore, in the example under consideration

$$dF = \mu_1 dN_1 + \mu_2 dN_2 \quad \dots(6.60)$$

where  $dN_1$  and  $dN_2$  are the changes in the number of particles on the two sides of the partition. If the composite system is closed,  $N_1 + N_2$  is constant.

Therefore  $dN_1 + dN_2 = 0$ ; or  $dN_1 = -dN_2$

$$\text{Hence } dF = (\mu_1 - \mu_2) dN_1 \quad \dots(6.61)$$

If the composite system is in the equilibrium state

$$\frac{\partial F}{\partial N_1} = \frac{\partial F}{\partial N_2} = 0 \quad \dots(6.62)$$

Therefore  $\mu_1 - \mu_2 = 0$ ;  $\mu_1 = \mu_2$   $\dots(6.63)$

We, therefore, conclude that if a system is to be in an equilibrium state, temperature, pressure and chemical potential must be constant throughout the system.

## 6.7 THERMODYNAMIC FUNCTIONS IN TERMS OF THE GRAND PARTITION FUNCTION

(i) **Entropy.** We write entropy in the form

$$S = -k \sum P_{N_i} \ln P_{N_i} \quad \dots(6.64)$$

$$\text{Now, } P_{N_i} = \frac{e^{-\beta(U_{N_i} - N\mu)}}{Z} \quad \dots(6.65)$$

$$\begin{aligned} \text{Therefore, } S &= -k \sum P_{N_i} \ln \left( \frac{e^{-\beta(U_{N_i} - N\mu)}}{Z} \right) \\ &= -k \sum P_{N_i} \left\{ -\beta U_{N_i} + \beta N\mu - \ln Z \right\} \\ &= k\beta \sum P_{N_i} U_{N_i} - k\beta \mu \sum P_{N_i} N + k \sum P_{N_i} \ln Z \\ &= k\beta \langle U \rangle - k\beta \langle N \rangle \mu + k \ln Z \end{aligned} \quad \dots(6.66)$$

The other relations defining thermodynamics potential take the following forms in respect of the grand canonical ensemble.

(ii) **Internal energy  $U$  at constant temperature and pressure**

$$U = TS - pV + \mu \sum N_i$$

$$\text{Therefore } dU = TdS - pdV + \mu \sum dN_i \quad \dots(6.67)$$

(iii) **Helmholtz free energy  $F$ :** This is useful in systems which are closed and thermally coupled to the outside world, but are mechanically isolated.  $F$  is obtained from  $U$  by adding a term due to thermal coupling

$$F = U - TS = \mu \langle N \rangle - pV \quad \dots(6.68)$$

- (iv) **Enthalpy  $H$ :** This is useful potential for systems which are thermally isolated and closed but mechanically coupled to the outside world.  $H$  is obtained by adding an additional energy, due to the mechanical coupling, to the internal energy  $U$ , given by

$$H = U + pV = \mu \langle N \rangle + TS \quad \dots(6.69)$$

- (v) **Gibbs free energy  $G$ :** This is obtained by adding terms due to thermal and mechanical couplings to the internal energy  $U$ , given by

$$G = U - TS + pV = \mu \langle E \rangle \quad \dots(6.70)$$

The above relations have been obtained for a  $p$ ,  $V$ ,  $T$  system. They could be generalized by introducing a generalized force  $Y$  (in place of  $p$ ) and a generalized displacement  $X$  (in place of  $V$ ). The relation (6.67) then would be replaced by

$$dU = Tds + YdX + \sum_i \mu dN_i \quad \dots(6.71)$$

## 6.8 IDEAL GAS

We shall derive in this section various thermodynamics properties of a classically ideal gas. As stated in the preceding section, an ideal gas is one in which mutual interactions between molecules are negligible, i.e. potential energy of interaction  $U = 0$ . This is a good approximation, particularly in the case of rarefied gases.

The total energy of an ideal gas consisting of  $N$  molecules each of mass  $m$  is

$$E = \sum_{i=1}^N P_i^2 / 2m \quad \dots(6.72)$$

We have seen that almost all the macroscopic properties of the systems can be calculated, once we have evaluated the partition function  $Z = \sum e^{-\beta E_s}$ . The summation here is over all the discrete states  $s$ . This implies that we are tacitly assuming the states to be discrete. In other words, we are dealing with quantized systems. For a classical system, where the states form a continuous spectrum, the sums must be replaced by integrals. How can one make a transition from summation to integration?

We have seen in Ch. 4, how the notion of phase space has been useful in specifying a state of a classical system. A cell in phase space in classical discussion is analogous to a state in quantum mechanical discussion. Therefore, for a classical system, a sum over states must be replaced by an integral over phase space.

Consider the phase space divided into cells each of value  $\hbar^f$ , where  $f$  is the number of degrees of freedom. Let  $dV = dq_1 \dots dq_f; dp_1 \dots dp_f$  be a volume element in the phase space at the point  $(q_1 \dots q_f, p_1 \dots p_f)$  the

energy throughout it being the same. The number of cells in this volume element is obviously  $\frac{dq_1 \dots dq_f, dp_1 \dots dp_f}{h^f}$ .

To find the partition function, we first sum over these cells and then integrate over all such elements of volume. Thus

$$Z = \int \dots \int e^{-\beta E} \frac{dq_1 \dots dq_f, dp_1 \dots dp_f}{h^f} \quad \dots(6.73)$$

In the case of the ideal gas under consideration, if  $N$  is the number of molecules, their position vector and  $f = 3N$

$$Z = \frac{1}{h^{3N}} \int \dots \int e^{-\beta \left( \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \dots \right)} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} \quad \dots(6.74)$$

Now

$$\int \dots \int dq_1 \dots dq_{3N} = \int d^3 q_1 \int d^3 q_2 \dots \int d^3 q_N = V^N \quad \dots(6.75)$$

where  $V$  is the volume of the container.

Therefore

$$\begin{aligned} Z &= \frac{V^N}{h^{3N}} \int \dots \int e^{-\beta \left( \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \dots \right)} dp_1 dp_2 \dots dp_{3N} \\ &= \frac{V^N}{h^{3N}} \int_{-\infty}^{\infty} e^{-\beta \frac{p_1^2}{2m}} d^3 p_1 \int_{-\infty}^{\infty} e^{-\beta \frac{p_2^2}{2m}} d^3 p_2 \dots \int_{-\infty}^{\infty} e^{-\beta \frac{p_N^2}{2m}} d^3 p_N \\ &= \frac{V^N}{h^{3N}} \left[ \int_{-\infty}^{\infty} e^{-\beta p^2/2m} d^3 p \right]^N \end{aligned} \quad \dots(6.76)$$

The integral inside the brackets is

$$\begin{aligned} \int_{-\infty}^{\infty} e^{-\beta p^2/2m} d^3 p &= \int_{-\infty}^{\infty} e^{-\beta p_x^2/m} dp_x \int_{-\infty}^{\infty} e^{-\beta p_y^2/m} dp_y \int_{-\infty}^{\infty} e^{-\beta p_z^2/m} dp_z \\ &= \left[ \int_{-\infty}^{\infty} e^{-\beta p^2/2m} dp \right]^3 = \left( \frac{2m\pi}{\beta} \right)^{3/2} \end{aligned} \quad \dots(6.77)$$

Therefore

$$Z = \frac{V^N}{h^{3N}} \left[ \frac{2m\pi}{\beta} \right]^{3/2} = \left[ \left( \frac{2m\pi kT}{\hbar^2} \right)^{3/2} V \right]^N \quad \dots(6.78)$$

The various thermodynamics quantities can be derived from this. Thus

$$\ln Z = N \left[ \ln V + \frac{3}{2} \ln \left( \frac{2\pi m}{h^2} \right) - \frac{3}{2} \ln \beta \right] \quad \dots(6.79)$$

Therefore (a)  $\langle p \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{N}{\beta V} = \frac{NkT}{V}$  ... (6.80)

or  $\langle p \rangle V = NkT$  ... (6.81)

the equation of state of the gas

(b)  $\langle E \rangle = \frac{\partial \ln Z}{\partial \beta} = \frac{3N}{2\beta} = \frac{3}{2} NkT$  ... (6.82)

(c)  $C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk$  ... (6.83)

(d)  $F = -kT \ln Z$

$$= kTN \left[ \ln V + \frac{3}{2} \ln \left( \frac{2\pi m}{h^2} \right) - \frac{3}{2} \ln \beta \right]$$

$$= -NkT \ln \left[ \left( \frac{2\pi m k T}{h^2} \right)^{3/2} V \right] \quad \dots(6.84)$$

(e)  $S = k[\ln Z + \beta \langle E \rangle]$

$$= Nk \left[ \ln V + \frac{3}{2} \ln \left( \frac{2\pi m}{h^2} \right) - \frac{3}{2} \ln \beta + \frac{3}{2} \right]$$

$$= Nk \left[ \ln V + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{2\pi m k}{h^2} \right) + \frac{3}{2} \right]$$

$$= Nk \left[ \ln V + \frac{3}{2} \ln T + \sigma \right] \quad \dots(6.85)$$

where

$$\sigma = \frac{3}{2} \left[ \ln \left( \frac{2\pi m k}{n^2} \right) + 1 \right] \quad \dots(6.86)$$

Note that because  $h$  is arbitrary the value of the constant in the expression (6.85) is indeterminable and, hence, the absolute value of entropy eludes us.

The thermodynamic functions given above are derived on the assumption that the molecules of the gas are distinguishable. However, it is easy to show that this assumption leads to results in contradiction with experience. We will show in the next section how the computation of entropy of a classical ideal gas from Eq. (6.85), leads to a paradoxical result for the case when two equal volumes of the same gas are mixed together.

## 6.9 GIBBS PARADOX

Suppose, there are two different ideal gases, one composed of  $N_1$  molecules and the other of  $N_2$  molecules. Let  $V_1$  and  $V_2$  be the volumes the two gases occupy. Suppose, further, that these gases are separated by a membrane as shown in Fig. 6.3 and they are at the same temperature and pressure.

If the membrane is now removed, the two gases will mix; but there will be no change in the energies of the two systems so long as the temperature remains the same. Let us now calculate the resulting change in entropy using Eq. (6.85).

The entropies of the two systems before mixing are

$$S_1 = N_1 k \ln V_1 + \frac{3}{2} N_1 k \left\{ 1 + \ln \left( \frac{2\pi m_1 k T}{h^2} \right) \right\} \quad \dots(6.87)$$

and

$$S_2 = N_2 k \ln V_2 + \frac{3}{2} N_2 k \left\{ 1 + \ln \left( \frac{2\pi m_2 k T}{h^2} \right) \right\} \quad \dots(6.88)$$



Fig. 6.3

The entropy of the composite system before mixing is given by

$$\sum_{i=1}^2 S_i = S_1 + S_2$$

After the partition is removed and diffusion is completed, the gases are mixed and occupy a volume  $V_1 + V_2$ , the temperature and pressure of the mixture remaining the same. The change in the entropy for each component in the process of mutual diffusion as obtained from Eqs. (6.87) and (6.88) is

$$\begin{aligned} \Delta S_1 &= N_1 k \ln (V_1 + V_2) - N_1 k \ln V_1 \\ &= N_1 k \ln \frac{V_1 + V_2}{V_1} \end{aligned} \quad \dots(6.89)$$

and

$$\Delta S_2 = N_2 k \ln \frac{V_1 + V_2}{V_2} \quad \dots(6.90)$$

Hence, the total change in the entropy of the system is

$$\Delta S = \Delta S_1 + \Delta S_2 = k \left[ N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right] \quad \dots(6.91)$$

which is positive and is known as the *entropy of mixing*.

This result is experimentally correct; when the membrane is removed the molecules of one gas diffuse into the region which was previously occupied by the other gas alone. The diffusion process is irreversible, for by reinserting the membrane into the system one would obtain two samples of the mixture and not the two gases that were originally present on mixing, therefore, the entropy of the combined system must increase.

However, a paradoxical situation arises when we consider the mixing of two samples of the same gas.

Suppose, two equal volumes of the same gas are at the same temperature and pressure and contain the same number of molecules (Fig. 6.4).



Fig. 6.4

Since in this case  $V_1 = V_2 = V; N_1 = N_2 = N$

$$\Delta S = 2kN \ln 2 \quad \dots(6.92)$$

This indicates that the removal of a partition between the equal volumes of the same gas causes an increase in the total entropy; which means that the entropy is not an extensive quantity. Further, one can imagine that the present state of the gas is arrived at by removing a number of membranes that initially divided the container into any number of compartments. Since there will be increase in entropy with every membrane removed, the entropy could be longer than any number.

This result in Eq. (6.92) is unacceptable because the mixing of the two samples considered above is a reversible process. We can insert the membrane back to its position in the system and obtain a situation which is in no way different from the one we had before mixing. The total entropy of the combined system, therefore, should not change. This paradox is known as *Gibbs paradox* since it was discussed first by Gibbs.

The paradox can be resolved only within the framework of quantum mechanics. The molecules of an ideal gas are indistinguishable. Therefore, a permutation of the  $N$  particles in a given state cannot alter the state of the gas. Thus, if we consider two configurations which differ from one another merely in the interchange of two molecules in different energy states, in view of the indistinguishability of the molecules, the configurations are not distinct; while according to our classical mode of counting we would regard them as two distinct configurations.

In the treatment of the classical ideal gas given in the proceeding section, we have, therefore, 'over counted' the states by assuming the molecules to be distinguishable and that permutation of  $N$  molecules

would lead to  $N!$  different states. In 'correct' counting their would be  $\frac{1}{N!}$  fewer states. The 'correct' translational partition function for the ideal gas, therefore is

$$Z = \frac{V^N}{N!h^{3N}} \left( \frac{2m\pi}{\beta} \right)^{3N/2} \quad \dots(6.93)$$

and not the one given by Eq. (6.78)

Therefore

$$\begin{aligned} \ln Z &= N \ln \left[ \left( \frac{2m\pi}{h^2\beta} \right)^{3/2} V \right] - \ln N! \\ &= N \left[ \ln V + \frac{3}{2} \ln \left( \frac{2m\pi}{h^2\beta} \right) \right] - N \ln N + N \end{aligned}$$

(by Stirling's formula)

$$\text{Therefore } \ln Z = N \left[ \ln \frac{V}{N} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + 1 \right] \quad \dots(6.94)$$

$$\begin{aligned} &= Nk \left[ \ln \frac{V}{N} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + 1 + \frac{3}{2} \right] \left( \text{because } E = \frac{3}{2} kT \right) \\ &= Nk \left[ \ln \frac{V}{N} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + \frac{5}{2} \right] \quad \dots(6.95) \end{aligned}$$

This equation is generally referred to as the *Sackur-Tetrode* equation. One can easily check that the entropy thus defined is a well-behaved extensive quantity.

From Eq. (6.95) the entropy of the two equal volumes of the same gas (Fig. 6.4) before mixing is

$$S_1 + S_2 = 2 Nk \left\{ \ln \frac{V}{N} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + \frac{5}{2} \right\} \quad \dots(6.96)$$

The entropy of the mixture as obtained from the same formula is the same as given by Eq. (6.96); since  $V$  and  $N$  are here doubled.

$$\text{Therefore } \Delta S = 0$$

The paradox, thus, is resolved.

It may be noted that the formula (6.95) for entropy does not affect the equation of state and the thermodynamic functions  $\langle p \rangle$ ,  $\langle E \rangle$  of a system as the term subtracted, viz.  $\ln N!$  is independent of  $T$  and  $V$ . Other functions which come out correctly from the modified expression for entropy are:

(1) Free energy  $F$  of a system is

$$F = -kT \ln Z = -kT N \left[ \ln \left\{ \frac{V}{N} \left( \frac{2m\pi}{h^2\beta} \right)^{3/2} \right\} + 1 \right]$$

$$= -kTN \ln \left[ \left( \frac{2m\pi}{h^2\beta} \right)^{3/2} \frac{Ve}{N} \right]$$

where  $e$  is the base of the Napierian logarithm; while Gibbs free energy is

$$(2) \quad G = E - TS + PV = F + PV$$

$$= -kTN \ln \left[ \left( \frac{wm\pi}{h^2\beta} \right)^{3/2} \frac{Ve}{N} \right] \quad \dots(6.97)$$

(3) Chemical potential  $\mu$  is given by

$$\mu N = G$$

Therefore  $\mu = -kTN \ln \left[ \left( \frac{2\pi m}{h^2\beta} \right)^{3/2} \frac{V}{N} \right] \quad \dots(6.98)$

## 6.10 THE EQUIPARTITION THEOREM

In the statistical treatment of a system, molecules, the mean energy of a molecule is of great importance. The treatment of mean energies becomes particularly simple when we can express the energy of a molecule as a sum of terms, one or more of which depend quadratically on a single variable out of the total set of variables  $q_1 \dots q_f, p_1 \dots p_f$ , where  $f$  is the number of degrees of freedom.

Let the energy of a molecule of a system, due to its motion in  $q_i$  direction be quadratic in momentum  $p_i$  i.e.  $\epsilon_i = \alpha p_i^2$ . Let its total energy be

$$E = \alpha p_i^2 + E' \quad \dots(6.99)$$

where  $E'$  does not depend upon  $p_i$  and the first term involves only the single variable  $p_i$ . If the system is in thermal equilibrium, the mean value of  $\epsilon_i$  is given by

$$\langle \epsilon \rangle = \frac{\int_{-\infty}^{\infty} e^{-\beta E(q_1 \dots p_f)} \alpha p_i^2 dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E(q_1 \dots p_f)} dq_1 \dots dp_f} \quad \dots(6.100)$$

Splitting  $E$  into two parts i.e.  $E = \alpha p_i^2 + E'$  we can write

$$\langle \epsilon \rangle = \frac{\int_{-\infty}^{\infty} e^{-\beta \alpha p_i^2} \alpha p_i^2 dp_i \int_{-\infty}^{\infty} e^{-\beta E'} dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta \alpha p_i^2} dp_i \int_{-\infty}^{\infty} e^{-\beta E'} dq_1 \dots dp_f} \quad \dots(6.101)$$

The last integrals in the numerator and denominator are  $f - 1$  fold integrals extending overall  $q$ 's and  $p$ 's excepts  $p_i$  and they are equal.

$$\text{Therefore } \langle \epsilon \rangle = \frac{\int_{-\infty}^{\infty} e^{-\beta \alpha p_i^2} p_i^2 dp_i}{\int_{-\infty}^{\infty} e^{-\beta \alpha p_i^2} dp_i} \quad \dots(6.102)$$

Substituting

$$\beta \alpha p_i^2 = y^2, \text{ i.e. } \sqrt{\beta} \alpha p_i = y$$

$$\text{We get } \langle \epsilon \rangle = \frac{\int_{-\infty}^{\infty} e^{-y^2} y^2 dy}{\beta \int_{-\infty}^{\infty} e^{-y^2} dy}$$

Using the standard formula of integration (See Appendix B, we get

$$\langle \epsilon \rangle = \frac{\sqrt{\pi}/2}{\beta \sqrt{\pi}} = \frac{1}{2\beta} = \frac{1}{2} kT \quad \dots(6.103)$$

If we had taken the energy in the  $q_i$  direction to be  $bq_i^2$ , we would have obtained a similar result. Thus, if a system is in thermal equilibrium, each term in the Hamiltonian that depends quadratically on a momentum or a coordinate, contributes a mean energy  $\frac{1}{2} kT$ . This is known as the *Principle of equipartition of energy*.

It must be emphasized here that this is not a general principle of statistical mechanics. It is a consequence of the assumption that the energy has a quadratic dependence on the variables involved. The *general equipartition principle* has been derived by Tolman in the form

$$\left\langle q_i \frac{\partial \epsilon}{\partial q_i} \right\rangle = \left\langle p_i \frac{\partial \epsilon}{\partial p_i} \right\rangle = kT \quad \dots(6.104)$$

One can easily check that when  $\epsilon$  depends quadratically on a variable, Eq. (6.104) reduces to Eq. (6.103).

### Examples

(i) **Mean kinetic energy of a molecule.** Kinetic energy of translation

$$E = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

$$\text{Therefore, } \langle E \rangle = 3 \times \frac{1}{2} kT = \frac{3}{2} kT \quad \dots(6.105)$$

(ii) **Three dimensional harmonic oscillator.** The Hamiltonian of the oscillator is

$$H = \sum_{i=1}^3 \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i=1}^3 kq_i^2$$

$$\text{Therefore } \langle E \rangle = 6 \times \frac{1}{2} kT = 3kT \quad \dots(6.106)$$

(iii) **Specific heat of solids.** Consider a gramme atom of a solid containing  $N_\alpha$  (Avogadro's number) non-interacting atoms harmonically bound to the centre of forces. The Hamiltonian of each atom is

$$H = \sum_{i=1}^3 \left( \frac{p_i^2}{2m} + \frac{1}{2} k q_i^2 \right)$$

The total energy, therefore, is the same as that of  $3N_\alpha$  independent one-dimensional oscillators.

$$\text{Therefore } E = N_\alpha \times 3kT = 3N_\alpha kT = 3RT \quad \dots(6.107)$$

The specific heat per gramme atom is

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3R \quad \dots(6.108)$$

which is Dulong-Petit law.

## 6.11 THE STATISTICS OF PARAMAGNETISM

In this section we treat the problem of paramagnetism classically. Its quantum mechanical treatment is given in Ch. 8.

In some crystals some of the atoms have a resultant magnetic dipole moment, associated with either electron orbital angular momentum or electron spin, or both. If such an atom is placed in a magnetic field, the magnetic moments tend to align themselves in the direction of the field. These atoms are *paramagnetic atoms*.

For simplicity let us consider a simplified model in which each paramagnetic atom has only one unpaired electron which is in a state of zero orbital angular momentum. Further, we neglect the interaction between the unpaired electrons. When a magnetic field is applied to the material, the electron spin angular momentum of each unpaired electron can have a component  $\hbar/2$  either parallel or antiparallel to the field. That is, each unpaired electron has a magnetic moment  $\mu$  equal to one Bohr magneton pointing either parallel or anti-parallel to the field. The potential energies of the magnetic dipoles in these two states are different.

### 6.11.1 Potential Energy of a Magnetic Dipole in a Magnetic Field

When a magnetic field induction  $\mathbf{B}$  is applied an atom which has its magnetic moment pointing at an angle  $\theta$  to the direction of the field, will experience a torque  $= \mu \times \mathbf{B}$ .

In Fig. 6.5, the magnetic dipole is pointing at an angle  $(90^\circ + \theta)$  to the direction of the field. The numerical value of the torque is  $\mu B \sin (90^\circ + \theta) = \mu B \cos \theta$ . The work done in rotating the magnetic dipole through an angle  $d\theta$  is

$$dW = \mu B \cos \theta \, d\theta \quad \dots(6.109)$$

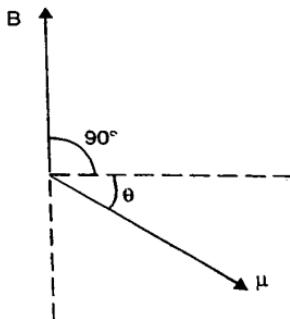


Fig. 6.5

The work done to rotate the magnetic dipole from  $\theta = 0$  to  $\theta = \pi/2$  i.e. in a direction opposite to that of the field is

$$W = \int_0^{\pi/2} \mu B \cos \theta d\theta \quad \dots(6.110)$$

The potential energy of the dipole in this position, therefore, is  $\mu B$ . In the same way we can show that the potential energy of the magnetic dipole when it points in the direction of the magnetic field is  $-\mu B$ .

### 6.11.2 Curie's Law

In an applied magnetic field each unpaired electron may be either in a state with energy  $\mu B$  or that with energy  $-\mu B$  (Fig. 6.6). We can apply Boltzmann distribution to the system by treating an unpaired electron as a sub-system and the rest of the crystal as a heat reservoir.

The partition function of the system is

$$Z = e^{\mu B/kT} + e^{-\mu B/kT} \quad \dots(6.111)$$

The probability that in thermal equilibrium, the magnetic dipole points parallel to the field is

$$P_1 = \frac{e^{\mu B/kT}}{Z} \quad \dots(6.112)$$

Similarly, the probability that it points antiparallel to the field is

$$P_2 = \frac{e^{-\mu B/kT}}{Z} \quad \dots(6.113)$$

If  $N$  is the total number of unpaired electrons in states (1) and (2), the populations of the two states are

$$\text{_____} \mu B$$

$$\text{_____} -\mu B$$

Fig. 6.6

$$N_1 = NP_1; N_2 = NP_2$$

and

$$\frac{N_2}{N_1} = \frac{P_2}{P_1} = e^{-2\mu B/kT} \quad \dots(6.114)$$

The mean magnetic moment parallel to the magnetic field is

$$\begin{aligned} \langle \mu \rangle &= \sum P_i \mu_i = P_1 \mu - P_2 \mu \\ &= \mu \left\{ \frac{e^{\mu B/kT} - e^{-\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}} \right\} \\ &= \mu \tan h (\mu B/kT) \quad \dots(6.115) \\ &\left( \text{because } \tan hy = \frac{e^y - e^{-y}}{e^y + e^{-y}} \right) \end{aligned}$$

If there are  $N$  independent non-interacting unpaired electrons in a sample, its mean magnetic moment is

$$\langle m \rangle = N \langle \mu \rangle = N\mu \tan h \frac{\mu B}{kT} \quad \dots(6.116)$$

If  $y \gg 1$ ,  $\tan h y \approx 1$ . Hence from Eq. (6.116) we see that if  $\frac{\mu B}{kT} \gg 1$  (which is the case when temperature is very low and magnetic field is very high), then

$$\langle m \rangle = N\mu \quad \dots(6.117)$$

This is easy to understand, because at low temperatures magnetic dipoles are in their lower energy states. Because of the high magnetic field they point in the direction of the field and the system, thus, reaches a state of a magnetic saturation.

If, on the other hand,  $y \ll 1$

$$\tan hy = \frac{1+y-1+y}{1+y+1-y}$$

Hence, if  $\frac{\mu B}{kT} \ll 1$ , i.e. at high temperature and low magnetic field,

$$\tan h \frac{\mu B}{kT} = \frac{\mu B}{kT}$$

and  $\langle m \rangle = \frac{N\mu^2 B}{kT} \quad \dots(6.118)$

Magnetization is defined as the magnetic moment per unit volume and is proportional to the field applied. If  $m$  (Eq. 6.118) corresponds to a unit volume of the material

$$m \propto b \text{ i.e. } m = \chi B \quad \dots(6.119)$$

where  $\chi$  is a constant known as *paramagnetic susceptibility*. If  $\chi$  is negative the substance is said to be *diamagnetic*. If it is positive and small the material is said to be *paramagnetic*.

From Eqs. (6.118) and (6.119) we see that

$$\chi = \frac{N\mu^2}{kT} = \frac{C}{T} \quad \dots(6.120)$$

i.e., susceptibility is inversely proportional to temperature. This is known as the *Curie law of paramagnetism* and  $C$  is called *Curie constant*, given by

$$C = \frac{N\mu^2}{k} \quad \dots(6.121)$$

In the treatment given above, we have considered only a simplified model in which each atom has spin  $1/2$ . We shall now discuss the general case of arbitrary spin.

Consider a substance in which each atom has an intrinsic magnetic moment  $\mu$ . When a magnetic field  $B$  is applied, any atom which has its magnetic moment pointing at an angle  $\theta$  to the direction of the field, will experience a torque tending to align it in the direction of the field and as a consequence will have a magnetic energy.

$$\epsilon(\theta) = -\mu B \cos \theta \quad \dots(6.122)$$

Now, the number of states available for atoms with their magnetic moment pointing at an angle  $\theta$  within an element of solid angle  $d\omega$  is proportional to  $d\omega$  i.e.

$$C d\omega = C \sin \theta d\phi$$

where  $C$  is a constant.

The mean value  $\langle \mu \rangle$ , therefore, is

$$\begin{aligned} \langle \mu \rangle &= \frac{\int_0^{2\pi} \int_0^\pi e^{\beta \mu B \cos \theta} \mu \cos \theta C \sin \theta d\theta d\phi}{\int_0^{2\pi} \int_0^\pi e^{\beta \mu B \cos \theta} C \sin \theta d\theta d\phi} \\ &= \frac{2\pi \mu \int_0^\pi e^{\beta \mu B \cos \theta} \cos \theta \sin \theta d\theta}{2\pi \int_0^\pi e^{\beta \mu B \cos \theta} \sin \theta d\theta} \end{aligned} \quad \dots(6.123)$$

Substituting

$$\beta \mu B \cos \theta = y$$

We obtain

$$\begin{aligned} \langle \mu \rangle &= \frac{\frac{\mu}{(\beta \mu B)^2} \int_{-\beta \mu B}^{\beta \mu B} e^y y dy}{\frac{1}{\beta \mu B} \int_{-\beta \mu B}^{\beta \mu B} e^y dy} \\ &= \frac{1}{\beta B} \left[ -\beta \mu B \frac{e^{-\beta \mu B} + e^{\beta \mu B}}{e^{-\beta \mu B} - e^{\beta \mu B}} - 1 \right] \end{aligned} \quad \dots(6.124)$$

If, now  $\beta \mu B \gg 1$  which is the case when magnetic field is strong or temperature low,  $= \mu \langle \mu \rangle$  which implies that the induced magnetic moment  $m$  will reach its maximum, or saturation value  $N\mu$ , independent of  $B$ , where  $N$  is the number of atoms per unit volume.

If, on the other hand,  $\beta \mu B \ll 1$  (temperature high or field low), the expansion of the exponential in terms involving  $(\beta \mu B)^3$  gives the approximation

$$\langle \mu \rangle = \frac{1}{3} \beta \mu^2 B \quad \dots(6.125)$$

$$\text{Therefore, } m = N \langle \mu \rangle = \frac{N \mu^2 B}{3kT} = \chi B \quad \dots(6.126)$$

and, thus

$$\chi = \frac{N\mu^2}{3kT} \quad \dots(6.127)$$

Alternatively (following Langevin), the partition function for the magnetic energy of the atoms is given by

$$Z_{mag} = \sum_{\theta} e^{-\beta \epsilon(\theta)} = \sum_{\theta} e^{\beta \mu B \cos \theta} \quad \dots(6.128)$$

Replacing summation by integration

$$\begin{aligned} Z_{mag} &= \int_0^{2\pi} \int_0^\pi e^{-\beta \mu B \cos \theta} \sin \theta d\theta d\phi \\ &= 2\pi \int_0^\pi e^{\beta \mu B \cos \theta} \sin \theta d\theta \\ &= \frac{2\pi}{\beta \mu B} (e^{\beta \mu B} - e^{-\beta \mu B}) \\ &= \frac{4\pi}{\beta \mu B} \sinh \beta \mu B \end{aligned} \quad \dots(6.129)$$

Now

$$\begin{aligned} \epsilon_{mag} &= -N \frac{\partial \ln Z_{mag}}{\partial \beta} = \frac{NkT^2}{Z_{mag}} \frac{\partial Z_{mag}}{\partial T} \\ &= \frac{NkT}{\sinh \frac{\mu B}{kT}} \left\{ \sinh \frac{\mu B}{kT} - \frac{\mu B}{kT} \cosh \frac{\mu B}{kT} \right\} \\ &= N \mu B \left\{ \frac{kT}{\mu B} - \coth \frac{\mu B}{kT} \right\} \end{aligned} \quad \dots(6.130)$$

Since

$$\epsilon_{mag} = -mB \quad \dots(6.131)$$

$$\begin{aligned} m &= -\frac{\epsilon_{mag}}{B} = N\mu \left\{ \coth \frac{\mu B}{kT} - \frac{kT}{\mu B} \right\} \\ &= N\mu L \left\{ \frac{\mu B}{kT} \right\} \end{aligned} \quad \dots(6.132)$$

where  $L(x)$  is the so-called *Langevin function*, given by

$$L(x) = \coth x - \frac{1}{x} \quad \dots(6.133)$$

with

$$x = \beta \mu B$$

As before, if  $x \gg 1$ ,  $L(x)$  is almost equal to unity and the system acquires a state of magnetic saturation

$$m = N\mu$$

If  $x \ll 1$ ,  $L(x)$  may be written as

$$L(x) = \frac{x}{3} - \frac{x^5}{45} + \dots \quad \dots(6.134)$$

In the lowest approximation, therefore

$$m = \frac{N\mu^2}{3kT} B$$

and the susceptibility

$$\chi = \frac{N\mu^2}{3kT} = \frac{C}{T} \quad \dots(6.135)$$

## 6.12 THERMAL DISORDER IN A CRYSTAL LATTICE

In a monatomic crystal lattice a disorder may arise due to the displacement of some of the atoms from their normal positions to interstitial positions by the thermal vibrations of the lattice.

Suppose that there are  $N$  normal lattice points in a given volume, there will also be  $N$  interstitial positions. If the number of interstitial atoms is  $n$ , and the energy required to remove an atom from its normal position to an interstitial position is  $\epsilon$ , the energy of the lattice will be  $n\epsilon$ , assuming its energy in its ordered ground state to be zero.

Now the total number of distinct ways in which these  $n$  atoms can be arranged, among the  $N$  interstitial positions, is  $\frac{N!}{n!(N-n)!}$ . The number of ways in which the remaining  $N - n$  atoms can be arranged among the  $N$  normal positions is also  $\frac{N!}{n!(N-n)!}$ .

Therefore, the weight of the configuration in which there are interstitial atoms is

$$W = \left[ \frac{N!}{n!(N-n)!} \right]^2 \quad \dots(6.136)$$

The resulting entropy  $S$  is

$$\begin{aligned} S &= k \ln W = k \ln \left[ \frac{N!}{n!(N-n)!} \right]^2 \\ &= 2k [\ln N! - \ln n! - \ln (N-n)!] \end{aligned} \quad \dots(6.137)$$

Using Stirling's formula

$$\begin{aligned} S &= 2k[N \ln N - N - n \ln n + n - (N-n) \\ &\quad \ln (N-n) + N - n] \\ &= 2k [N \ln N - n \ln n - (N-n) \ln (N-n)] \end{aligned} \quad \dots(6.138)$$

Free energy of the lattice is

$$\begin{aligned} F &= E - TS \\ &= n\epsilon - 2kT [N \ln N - n \ln n - (N-n) \\ &\quad \ln (N-n)] \end{aligned} \quad \dots(6.139)$$

For the system to be in equilibrium configuration  $n$  must be such that  $F$  is minimum i.e.  $\frac{\partial F}{\partial n} = 0$

Therefore

$$\begin{aligned}\frac{\partial F}{\partial n} &= \epsilon - kT [-\ln n - 1 + 1 + \ln(N-n)] \\ &= \epsilon - 2kT [\ln(N-n) - \ln n] = 0 \quad \dots(6.140)\end{aligned}$$

Therefore  $\ln \frac{N-n}{n} = \frac{\epsilon}{2kT} = \frac{1}{2} \beta \epsilon \quad \dots(6.141)$

or  $n = \frac{N}{1 + e^{\frac{1}{2} \beta \epsilon}} \quad \dots(6.142)$

### 6.13 NON-IDEAL GASES

We have shown in Section 6.8 how Gibbs distribution can be applied to ideal gases. We will now show how it can be applied to real gases, in which account is taken of the interaction between the constituent atoms or molecules. The problem cannot be solved exactly, but even an approximate approach leads to results closer to experimental observations. Consider a relatively simple physical system, a monatomic gas of  $N$  identical atoms, each of mass  $m$ . The energy of the gas consisting of these interacting atoms is given by

$$\epsilon = \sum_{i=1}^N \frac{P_i^2}{2m} + U \quad \dots(6.143)$$

where the first term gives the kinetic energy of the atoms and  $U$  is the sum of the potential energies of interaction between the pairs of atoms, i.e.

$$U = u_{12} + u_{13} \dots + u_{23} + \dots = \frac{1}{2} \sum_{i \neq j} u_{ij} \quad \dots(6.144)$$

where  $u_{ij}$  is potential energy of interaction of  $i$ th and  $j$ th atoms. The factor  $\frac{1}{2}$  takes into account the fact that in the sum over  $i$  and  $j$ , the energy of interaction between each pair of atoms is counted twice.

The partition function  $Z$  is given by

$$\begin{aligned}Z &= \frac{1}{\hbar^{3N} N!} \int \dots \int e^{-\frac{\beta}{2m}(P_1^2 + P_2^2 + \dots + P_N^2)} d^3 p_1 d^3 p_2 d^3 \dots d^3 p_N \\ &\times \int \dots \int e^{\beta U} d^3 q_1 d^3 q_2 \dots d^3 q_N \quad \dots(6.145)\end{aligned}$$

The first integral is the same as derived for the ideal gases and is equal to

$$\frac{1}{h^{3N} N!} (2\pi m k T)^{3N/2} \quad \dots(6.146)$$

We will now evaluate the second integral

$$Z_u = \int \dots \int e^{-\beta U} d^3 q_1 \dots d^3 q_N \quad \dots(6.147)$$

If  $U = 0$  as in the case of an ideal gas

$$Z_u = V^N \quad \dots(6.148)$$

where  $V$  is the volume of the container.

In the case of non-ideal gases, the mean potential energy is

$$\langle U \rangle = \frac{1}{2} N (N - 1) \langle u \rangle = \frac{1}{2} N^2 \langle u \rangle \quad \dots(6.149)$$

where  $\langle u \rangle$  is the mean energy between a pair of atoms. The integrated energy is a function of the distance between two atoms  $r$ . The probability that an atom is at a relative distance  $r$  is

$$\frac{e^{-\beta u(r)}}{\int e^{-\beta u(r)} d^3 r_1 \dots d^3 r_N}$$

Therefore

$$\begin{aligned} \langle u \rangle &= - \frac{\int e^{-\beta u(r)} u(r) d^3 r}{\int e^{-\beta u(r)} d^3 r} \\ &= - \frac{\partial}{\partial \beta} \ln \int e^{-\beta u(r)} d^3 r \end{aligned} \quad \dots(6.150)$$

Now the integral

$$\begin{aligned} \int e^{-\beta u(r)} d^3 r &= \int \left[ 1 + \left( \int e^{-\beta u(r)} - 1 \right) \right] d^3 r \\ &= \int d^3 r + \int \left( e^{-\beta u(r)} - 1 \right) d^3 r \\ &= V + I(\beta) = V \left( 1 + \frac{I(\beta)}{V} \right) \end{aligned} \quad \dots(6.151)$$

where  $V$  is the volume of the container and

$$I(\beta) = \int \left( e^{-\beta u(r)} - 1 \right) d^3 r \quad \dots(6.152)$$

Therefore

$$\begin{aligned} \langle u \rangle &= - \frac{\partial}{\partial \beta} \ln \left\{ V \left( 1 + \frac{I(\beta)}{V} \right) \right\} \\ &= - \frac{\partial \ln V}{\partial \beta} - \frac{\partial}{\partial \beta} \ln \left( 1 + \frac{I(\beta)}{V} \right) \\ &= \frac{\partial}{\partial \beta} \ln \left( 1 + \frac{I(\beta)}{V} \right) \end{aligned}$$

$$= \frac{1}{1 + \frac{I(\beta)}{V}} \frac{\partial}{\partial \beta} \left( \frac{I(\beta)}{V} \right) \approx - \frac{1}{V} \frac{\partial I(\beta)}{\partial \beta} \quad \dots(6.153)$$

(because  $I(\beta) \ll V$ )

Hence

$$\langle U \rangle = \frac{1}{2} N^2 \langle u \rangle = - \frac{1}{2} \frac{N^2}{V} \frac{\partial I(\beta)}{\partial \beta} \quad \dots(6.154)$$

Integrating

$$\int_0^\beta \langle U \rangle d\beta = - \frac{1}{2} \frac{N^2}{V} I(\beta) + C$$

when  
gives

$$\begin{aligned} \beta &= 0 \quad I(0) = 0 \\ C &= 0 \end{aligned}$$

$$\text{Therefore } \int_0^\beta \langle U \rangle d\beta = - \frac{1}{2} \frac{N^2}{V} I(\beta) \quad \dots(6.155)$$

The mean potential energy  $\langle U \rangle$  can also be found from the relation

$$\begin{aligned} \langle U \rangle &= \frac{\int e^{-\beta U} U d^3 r_1 \dots d^3 r_N}{\int e^{-\beta U} d^3 r_1 \dots d^3 r_N} \\ &= - \frac{\partial}{\partial \beta} \ln Z_u \end{aligned}$$

$$\int_0^\beta \langle U \rangle d\beta = - \ln Z_u + C^1 \quad \dots(6.156)$$

$$\begin{aligned} \text{For } \beta &= 0, Z_u = V^N \\ C^1 &= \ln V^N = N \ln V \end{aligned}$$

From Eq. (6.156)

$$\begin{aligned} \ln Z_u &= N \ln V - \int_0^\beta \langle U \rangle d\beta \\ &= N \ln V + \frac{1}{2} \frac{N^2}{V} I(\beta) \end{aligned} \quad \dots(6.157)$$

where we have used Eq. (6.155).

The mean pressure  $\langle P \rangle$  is given by

$$\langle P \rangle = \frac{1}{\beta} \frac{\partial}{\partial V} (\ln Z_u) = \frac{1}{\beta} \cdot \frac{N}{V} - \frac{N^2 I(\beta)}{2 \beta V^2} \quad \dots(6.158)$$

$$\text{Therefore } \frac{\langle P \rangle}{kT} = n - \frac{1}{2} n^2 I(\beta)$$

where  $n = \frac{N}{V}$  is the concentration.

The equation of state for real gases is usually written in the form

$$\frac{\langle P \rangle}{kT} = n + B_2(T)n^2 + B_3(T)n^3 + \dots \quad \dots(6.159)$$

where the right-hand side is the series expansion in powers of  $n$  and is known as the *virial expansion*.  $B_2(T)$ ,  $B_3(T)$  etc., are the *virial coefficients* which vanish for an ideal gas. Comparing Eqs. (6.158) and (6.159) we find that

$$\begin{aligned} B_2 &= -\frac{1}{2} I(\beta) = -\frac{1}{2} \int (e^{-\beta u(r)} - 1) d^3r \\ &= -\frac{1}{2} \int (e^{-\beta u(r)} - 1) 4\pi r^2 dr \\ &= -2\pi \int (e^{-\beta u(r)} - 1) r^2 dr \end{aligned} \quad \dots(6.160)$$

For the evaluation of this integral we must the exact form of the interaction energy  $u(r)$ , which is a complicated function of  $r$ . Qualitatively the function should have the shape shown in Fig. 6.6. At larger distances the atoms virtually do not interact and their interaction energy may be taken to be zero. At smaller distances, forces of mutual attraction tend to bring the atoms closer and their interaction energy diminishes. At a distance  $r_0$ , the energy is minimum. At distances less than  $r_0$ , electron shells of the atoms begin to overlap, repulsive forces come into play and the potential energy increases.

There are no universal expressions for  $u(r)$ , suitable for all molecules. Usually  $u(r)$  is approximated by the formula

$$u(r) = \frac{a_1}{r^n} - \frac{a_2}{r^m} \quad \dots(6.161)$$

where the constants  $a_1$ ,  $a_2$  are so adjusted as to make the function a better approximation to a real potential. An analysis of potentials revealed that the following expression known as Lennard-Jones 6-12 potential has the shape shown in Fig. 6.6 and is the best approximation:

$$u(r) = u_0 \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right] \quad \dots(6.162)$$

For the present approximate treatment, however, we shall use a still simpler potential, viz.

$$u(r) = \begin{cases} \infty & \text{for } r < r_0 \\ -u_0 \left( \frac{r_0}{r} \right)^6 & \text{for } r > r_0 \end{cases} \quad \dots(6.163)$$

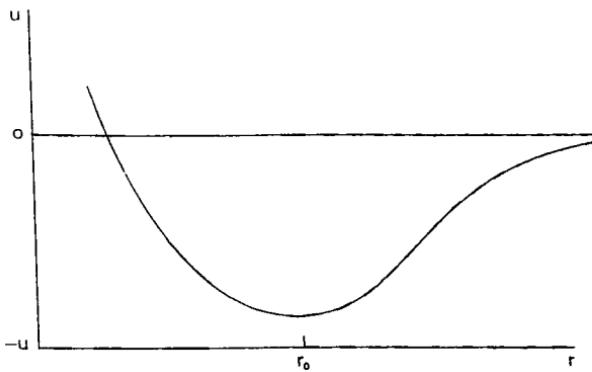


Fig. 6.7

which has the shape shown in Fig. 6.7. Now from Eq. (6.160)

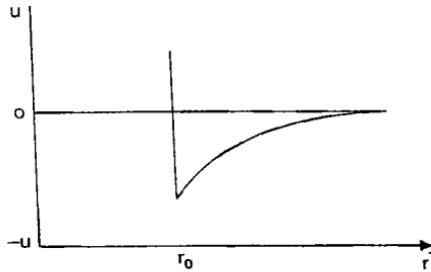


Fig. 6.8

$$\begin{aligned}
 B_2 &= -2\pi \int_0^{\infty} (e^{-\beta u(r)} - 1) r^2 dr \\
 &= -2\pi \left[ \int_0^{\infty} (e^{-\beta u(r)} - 1) r^2 dr + \int_0^{\infty} (e^{-\beta u(r)} - 1) r^2 dr \right] \dots(6.164)
 \end{aligned}$$

When  $r$  is small,  $u(r)$  is large and  $e^{-\beta u(r)} \rightarrow 0$

Therefore

$$B_2(T) = 2\pi \int_0^{r_0} r^2 dr - 2\pi \int_0^{\infty} (e^{-\beta u(r)} - 1) r^2 dr \dots(6.165)$$

Further, if the temperature is high  $\beta(u) \ll 1$  and  $e^{-\beta u(r)} = 1 - \beta u(r)$   
Hence

$$\begin{aligned}
 B_2(T) &= \frac{2\pi r_0^3}{3} + 2\pi \beta \int_{r_0}^{\infty} u(r) r^2 dr \\
 &= \frac{2\pi r_0^3}{3} - 2\pi \beta u_0 \int_{r_0}^{\infty} \frac{r_0^6}{r^4} dr
 \end{aligned}$$

$$= \frac{2\pi r_0^3}{3} - \frac{2\pi \beta u_0 r_0^3}{3} = \frac{2\pi r_0^3}{3} \left( 1 - \frac{u_0}{kT} \right) \quad \dots(6.166)$$

where we have used Eq. (6.163).

Let

$$b^1 = \frac{2\pi r_0^3}{3} \text{ and } \alpha^1 = \frac{2\pi r_0^3}{3} u_0 = b^1 u_0 \quad \dots(6.167)$$

$$\text{Therefore } B^2(T) = b^1 - \frac{\alpha^1}{kT} \quad \dots(6.168)$$

From Eq. (6.159), neglecting higher powers

$$\frac{\langle p \rangle}{kT} = n - B_2(T) n^2$$

$$\text{i.e. } \langle p \rangle = nkT + (b^1 kT - \alpha^1)n^2$$

$$\text{or } \langle p \rangle + \alpha^1 n^2 = nkT (1 + b^1 n)$$

$$= \frac{nkT}{1 - b^1 n}$$

where we have assumed that  $b^1 n \ll 1$ .

Hence

$$\text{or } (\langle p \rangle + \alpha^1 n^2) (1 + b^1 n) = nkT$$

$$\text{or } (\langle p \rangle + \alpha^1 n^2) \left( \frac{1}{n} - b^1 \right) = kT$$

Since  $n = \frac{N}{V} = \frac{N_A}{vd}$ , where  $N_A$  is the Avogadro's number and  $v$  molar volume, we have

$$\left( \langle p \rangle + \frac{\alpha^1 N_A^2}{v^2} \right) \left( \frac{v}{N_A} - b^1 \right) = kT$$

$$\text{or } \left( \langle p \rangle + \frac{a}{v^2} \right) (v - N_A b^1) = N_A kT$$

$$\text{i.e. } \left( \langle p \rangle + \frac{1}{v^2} \right) (v - b) = RT \quad \dots(6.169)$$

where we have put  $a = \alpha^1 N_A$ ,  $b = N_A b^1$  and  $R = N_A k$ .

Equation (6.169) is van der Waal's equation of state for real gases.

**PROBLEMS**

- 6.1** A cylinder of height  $l$  and base radius  $R$ , contains  $N$  molecules of an ideal gas each of mass  $m$ . The cylinder rotates with an angular velocity  $\omega$  about its axis. Calculate the pressure of the gas on the surface of the cylinder.
- 6.2** Calculate the internal energy of one litre of helium under a pressure  $9.8 \times 10^4 \text{ Pa}$  and temperature  $100^\circ\text{C}$ .
- 6.3** Establish the relations:
- $E = \left\{ \frac{\partial(\beta F)}{\partial \beta} \right\}_V$
  - $C_V = k\beta^2 \left\{ \frac{\partial^2(\beta F)}{\partial \beta^2} \right\}_V$
- where  $F$  is the free energy.
- 6.4** Prove that  $N = kT \frac{\partial \ln Z}{\partial \mu}$   
where  $\mu$  is the chemical potential.
- 6.5** Show that the entropy of a system in a grand canonical ensemble can be written as  $S = -k \sum P_r \ln P_r$ ,
- where  $P_r = \frac{Z^{N_r} e^{-\beta E_r}}{\sum_s Z^{N_s} e^{-\beta E_s}}$
- 6.6** A ferromagnetic system consists of  $N$  magnetic atoms each with spin  $\frac{1}{2}$ . What will be its entropy at
- absolute zero of temperature?
  - a very high temperature?
- 6.7** A system consisting of  $N$  spatially separated sub-systems, is in thermal equilibrium with a heat reservoir at absolute temperature  $T = \frac{\epsilon}{k}$ , where  $\epsilon$  is the energy. If each sub-system has non-degenerate energy levels of energy 0,  $\epsilon$ ,  $2\epsilon$ ,  $3\epsilon$  find
- the partition function,
  - the mean energy, and
  - the entropy of the system.
- 6.8** Consider a system of  $N$  one-dimensional harmonic oscillators. Treating the oscillators classically, obtain the expressions for (i) Helmholtz free energy, (ii) entropy and (iii) chemical potential of the systems.
- 6.9** Find the entropy of a mole of helium gas at  $T = 273 \text{ K}$  and pressure equal to one atmosphere. The mass of the helium atom is  $6.65 \times 10^{-27} \text{ kg}$ .

- 6.10** The mass of an argon atom is  $6.64 \times 10^{-26}$  kg. Find the chemical potential of a mole of argon at  $T = 273$  K and  $P = 1$  atmosphere.
- 6.11** You are given two vessels of equal volume. One contains a mole of gas A and the other a mole of gas B, the molecular weight of A being 10 times that of B. If the gas A is at temperature 300 K, calculate the temperature of B so that the two gases have the same entropy.
- 6.12** Show that the Sackur-Tetrode equation may also be written in the form.

$$S = Nk \left\{ -\ln p + \frac{5}{2} \ln T + \frac{3}{2} \ln \frac{2m\pi}{h^2} + \frac{5}{2} (\ln K + 1) \right\}$$

where  $p$  is the pressure of the ideal gas.

- 6.13** The temperature of an ideal monatomic gas is changed from  $T_1$  to  $T_2$ , keeping (i) its pressure constant, and (ii) its volume constant. Show that the ratio of the change in entropy  $\Delta S_p$  in case (i) to that of  $\Delta S_v$  in case (ii) is  $5/3$ .
- 6.14** A thermally insulated container is divided by a partition into two compartments, which contain identical gases at the same temperature and with equal number of particles,  $N$ , but at different pressures  $P_1$  and  $P_2$ . The partition is now removed. Calculate the total change in entropy.
- 6.15** Air is formed artificially by mixing four moles of nitrogen and one mole of oxygen at NTP. Calculate the entropy of mixing.



# FORMULATION OF QUANTUM STATISTICS

Although the ensemble theory developed so far is extremely general, we have considered its application only to some classical systems in which the components are considered distinguishable. But most of the quantum mechanical systems comprise indistinguishable components. The microparticles of the same species are indistinguishable from one another. All electrons are identical. If two electrons interchange places, the physical situation will not change. Hence, the rules for counting the microstates must be different from those used in the Maxwell-Boltzmann model. It is, therefore, necessary to treat the theory in terms of quantum mechanical wavefunctions and operators. The behaviour of the systems, treated in this way, generally differs from that expected from classical treatment. However, it will be shown later, that the dissimilarity in the behaviour gradually disappears in the limit of high temperatures and low densities.

## 7.1 DENSITY MATRIX

In classical statistical mechanics we specify the state of system by a point in the phase space and ensemble by a cloud. The mean value of any function  $F(q, p)$  is given by

$$\langle F \rangle = \int \dots \int F(q, p) \rho \, dq_1 \dots dp_f \quad \dots(7.1)$$

where  $\rho$  is the density of distribution of phase points and  $f$  the number of degrees of freedom.

Von Neumann has shown that a quantity called density matrix in quantum statistics takes the place of the distribution function in classical statistics. A knowledge of this matrix enables us to calculate the mean values of any quantity, describing a property of the system as well as the probabilities of various values of such quantities.

In quantum statistics the concept of uncertainty enters the discussion in two entirely different ways:

(1) Consider a large number of identical systems, all in the same quantum state. If one tries to assess the value of a dynamical variable corresponding to an operator  $\hat{O}$ , by performing the same measurement on all such systems, then each system will respond by jumping into one of the eigenstates of  $\hat{O}$  although it is quite impossible to predict in advance which eigenstate it is going to be. Consequently, such a set of measurements can only provide us with a probability distribution of the eigenvalues or the observable of the operator  $\hat{O}$ . This type of uncertainty forms an integral part of quantum mechanics and cannot be overcome by any conceivable refinement in the techniques of measurement. It is independent of our subjective lack of information or ignorance.

The Schrödinger equation

$$\hat{H}\Psi(q, t) = i\hbar \frac{\partial\Psi(q, t)}{\partial t} \quad \dots(7.2)$$

determines the variation of  $\Psi$  with time.

Let  $\{\phi_n(q)\}$  be a complete set of orthonormal functions of the system. Suffix  $n$  denotes the set of all quantum numbers which distinguish the various stationary states.  $\Psi(q, t)$  can be expressed as the linear combination of  $\phi_n(q)$ . Thus

$$\Psi(q, t) = \sum_n C_n(t) \phi_n(q) \quad \dots(7.3)$$

where  $C_n$ 's are the probability amplitudes for the system, i.e.

$$C_n^*(t)C_n(t) = |C_n(t)|^2$$

is the probability that the system, at time  $t$ , is in the state represented by  $\phi_n(q)$ . It is obvious that

$$\sum_n C_n^*(t)C_n(t) = \sum_n |C_n(t)|^2 = 1 \quad \dots(7.4)$$

The average value of an observable  $F$  for a system is given by

$$\langle F \rangle = \int \Psi^*(q, t) \hat{F} \Psi(q, t) dq \quad \dots(7.5)$$

where  $\hat{F}$  is the operator corresponding to the observable.

Using Eq. (7.3)

$$\begin{aligned} \langle F \rangle &= \int \sum_n C_n^*(t) \phi_n^*(q) \hat{F} \sum_m C_m(t) \phi_m(q) dq \\ &= \sum_{m,n} C_n^*(t) C_m(t) \int \phi_n^*(q) \hat{F} \phi_m(q) dq \\ &= \sum_{m,n} C_n^*(t) C_m(t) F_{nm} \end{aligned} \quad \dots(7.6)$$

where

$$F_{nm} = \int \phi_n^*(q) \hat{F} \phi_m(q) dq \quad \dots(7.7)$$

(2) There is another type of uncertainty, which is widely used in classical and quantum statistical mechanics and which expresses our lack of accurate knowledge about a system. Imagine a system which has a number of degrees of freedom. It is virtually impossible to carry out experiments to measure the values of each variable and thus determine the state of the system completely. The system then could be described approximately by specifying the mean values and corresponding probabilistic distributions of each variable.

If  $\langle F_\alpha \rangle$  is the mean value of the observable for the  $\alpha$ th system, the mean of this observable for  $N$  systems  $\alpha = 1, 2, \dots, N$ , is

$$\begin{aligned} \langle \bar{F} \rangle &= \frac{1}{N} \sum_{\alpha=1}^N \langle F_\alpha \rangle \\ &= \frac{1}{N} \sum_{\alpha=1}^N \left[ \sum_{m,n} C_n^{\alpha*}(t) C_m^\alpha(t) F_{nm} \right]. \end{aligned} \quad \dots(7.8)$$

This averaging has two-fold nature. It comprises averaging due to the probabilistic nature of the quantum description as well as statistical averaging. It may be noted that the entire averaging process is to be carried out as a single operation; its constituents cannot be separated.

Consider a system ( $\alpha$ th) whose state can be described in terms of probability amplitudes  $C_n^\alpha(t)$ . Then

$$\overline{C_n^*(t) C_m(t)} = \frac{1}{N} \sum_{\alpha=1}^N C_n^{\alpha*} C_m^\alpha(t) = \rho_{nm} \quad \dots(7.9)$$

is the mean value of the quantity  $C_n^*(t) C_m(t)$  over all the systems in the ensemble. We consider  $\rho_{mn}$  as the matrix element of statistical operator, viz. *density operator*—  $\hat{\rho}(t)$ . The term density refers to the fact that the diagonal element  $\rho_{nn} = |C_n(t)|^2$  of the matrix represents the probability that a system is found in the state defined by the function  $\phi_n(q)$ . The elements of the density matrix depend on the representation. The final result, however, must be independent of the representation.

Let us now see how the density matrix can be used to calculate the mean value of any observable  $F$  for the systems of an ensemble.

For a single system, the mean value of  $F$  is, by Eq. (7.6)

$$\langle F \rangle = \sum_{n,m} F_{nm} C_n^*(t) C_m(t)$$

Therefore, the mean value of  $F$  for all the systems in the ensemble

$$\langle F \rangle = \sum_{n,m} F_{nm} \overline{C_n^*(t) C_m(t)} = \sum_{m,n} F_{nm} \rho_{mn} \quad \dots(7.10)$$

This is the quantum mechanical analogue of the classical expression for the mean given by Eq. (7.1). Following the rules of matrix multiplications, we can write the foregoing equation as

$$\langle \overline{F} \rangle = \sum_n [F\rho]_{nn} = \sum_m [\rho F]_{nm} = \text{trace} [\hat{\rho} \hat{F}] \quad \dots(7.11)$$

Thus the integral over all of phase space of a classical quantity is replaced in quantum mechanics by the trace of the corresponding quantum mechanical matrix. This formula has the advantage of enabling us to calculate with any complete set of orthonormal wave functions.

Now if  $\hat{F} = \hat{I}$  the unit operator

$$\text{trace } \hat{\rho} = 1$$

$$\text{i.e.} \quad \sum_n C_n^*(t) C_n(t) = \sum_n |C_n(t)|^2 = 1 \quad \dots(7.12)$$

This is consistent with Eq. (7.4).

Therefore, the probability that the system lies in the  $n$ th state, corresponds to the diagonal element  $\rho_{nn}$  and the problem of determining the statistical distribution amounts to a calculation of the probabilities  $\rho_{nn}$ .

## 7.2 LIOUVILLE'S THEOREM IN QUANTUM STATISTICAL MECHANICS

Let us investigate the rate of change of the element  $\rho_{mn}$  with time.

$$\rho_{mn} = \frac{1}{N} \sum_{\alpha=1}^N C_n^{*\alpha}(t) C_m^\alpha(t)$$

$$\text{Therefore} \quad \dot{\rho}_{nn} = \frac{1}{N} \sum_{\alpha=1}^N [\dot{C}_n^{\alpha*}(t) C_m^\alpha(t) + C_n^{*\alpha}(t) \dot{C}_m^\alpha(t)] \quad \dots(7.13)$$

Now

$$\Psi^\alpha(q, t) = \sum_i C_l^\alpha \phi_l(q)$$

Multiplying both sides with  $\phi_n^*(q)$  and integrating over the entire range of  $q$

$$\int \phi_n^*(q) \Psi^\alpha(q, t) dq = \sum_i C_l^\alpha(t) \int \phi_n^*(q) \phi_l(q) dq \quad \dots(7.14)$$

$$\text{Therefore} \quad \dot{C}_n^\alpha(t) = \int \phi_n^*(q) \dot{\Psi}^\alpha(q, t) dq$$

$$= \frac{1}{i\hbar} \int \phi_n^*(q) \hat{H} \Psi^\alpha(q, t) dq$$

$$\begin{aligned}
 &= \frac{1}{i\hbar} \int \phi_n^*(q) \hat{H} \sum_i C_l^\alpha(t) \phi_l(q) dq \\
 &= \frac{1}{i\hbar} \sum_l H_{nl} C_l^\alpha(t)
 \end{aligned} \quad \dots(7.15)$$

and  $\dot{C}_l^{\alpha*}(t) = \frac{1}{-i\hbar} \sum_l H_{nl}^* C_l^{\alpha*}(t)$  ... (7.16)

Hence  $\rho_{mn} = \frac{1}{N} \sum_{\alpha=1}^N \left[ -\frac{1}{i\hbar} \left\{ \sum_l H_{nl}^* C_l^{\alpha*}(t) \right\} C_m^\alpha(t) \right]$

$$+ \frac{1}{i\hbar} \left\{ C_l^{\alpha*}(t) \left\{ \sum_l H_{ml} C_l^\alpha(t) \right\} \right\}$$

Since  $H_{ln} = H_{nl}^*$

$$\rho_{mn} = \frac{1}{i\hbar} \left[ \sum_l H_{ml} \rho_{ln} - \sum_l \rho_{ml} H_{ln} \right] \quad \dots(7.17)$$

Therefore  $i\hbar \dot{\rho}_{mn} = [\hat{H}\hat{\rho} - \hat{\rho}\hat{H}]$  ... (7.18)

i.e.  $i\hbar \dot{\rho} = [\hat{H}, \hat{\rho}]$  ... (7.19)

This is the quantum mechanical analogue of Liouville's theorem.

### 7.3 CONDITION FOR STATISTICAL EQUILIBRIUM

If the given system is in equilibrium, the corresponding ensemble must be stationary; i.e.  $\dot{\rho}_{mn} = 0$ . In analogy with classical mechanics, this would be possible, under the following conditions:

- (i) when the density matrix is constant, or
- (ii) when the density matrix is a function of a constant of motion.
- (iii) If the density matrix is constant, its elements will be given by

$$\rho_{mn} = \rho_0 \delta_{mn} \quad \dots(7.20)$$

i.e., all the non-diagonal elements of the matrix will be equal to zero and all the diagonal elements will be equal to a constant  $\rho_0$ .

Now in the energy representation, the basic function  $\phi_n$  are the eigenfunctions of the Hamiltonian  $\mathbf{H}$  and, hence, the matrices  $H$  and  $\rho$  are diagonal, i.e.

$$\rho_{mn} = \rho_n \delta_{mn} \quad \dots(7.21)$$

In this representation, the density operator  $\hat{\rho}$  may be formally written as

$$\hat{\rho} = \sum_n |\phi_n \rangle \rho_n \langle \phi_n| = [\hat{H}_1 \hat{\rho}] \quad \dots(7.22)$$

To verify this, consider an element  $\rho_{kl}$

$$\begin{aligned} \rho_{kl} &= \langle \phi_k | \hat{\rho} | \phi_l \rangle = \sum_n (\phi_k | \phi_n \rangle) \rho_n (\phi_n | \phi_l \rangle) \\ &= \sum_n \delta_{kn} \rho_n \delta_{nl} = \rho_k \delta_{kl} \end{aligned}$$

which agrees with Eq. (7.21).

Therefore

$$\begin{aligned} i\hbar \dot{\rho}_{mn} &= \sum_l [H_{ml} \rho_{ln} - \rho_{ml} H_{ln}] \\ &= \sum_l [\rho_0 H_{ml} \delta_{ln} - \rho_0 \delta_{ml} H_{ln}] \\ &= \rho_0 [H_{mn} - H_{nn}] = 0 \end{aligned}$$

The distribution, therefore, does not change with time and the system, under this condition is in equilibrium.

(ii) We see from Eq. (7.19), that if the time derivative of the statistical matrix vanishes, the operator  $\hat{\rho}$  must commute with  $\hat{H}$ . Hence  $\rho$  must be a function of a constant of motion.

## 7.4 ENSEMBLES IN QUANTUM MECHANICS

(i) **The microcanonical ensemble.** The systems constituting this ensemble are characterised by a fixed number of particles  $N$ , a fixed volume  $V$  and energy lying within the interval  $E$  and  $E + \delta E$ . The total number of accessible states to a system is say,  $\Omega(E)$ . In the energy representation the density matrix  $\rho$  will be a diagonal matrix, i.e.

$$\begin{aligned} \rho_{mn} &= \rho_0 \delta_{mn} \text{ for the states in the energy range} \\ &\quad E \text{ to } E + \delta E \\ &= 0 \text{ for all other states} \quad \dots(7.23) \end{aligned}$$

The trace of  $\rho$  is equal to the number of states whose energy lies between  $E$  and  $E + \delta E$ , i.e.

$$\text{Trace } \hat{\rho} = \sum_n \rho_0 = \Omega(E) \quad \dots(7.24)$$

The entropy, which determines the thermodynamics of the system, is given by

$$S = k \ln \Omega(E) \quad \dots(7.25)$$

Gibbs paradox does not arise in this case as  $\delta/\Omega(E)$  is supposed to be computed correctly by considering the indistinguishability of the particles.

Now if  $\Omega(E) = 1$ ,  $S = 0$  which is consistent with the Nernst theorem—Third law of Thermodynamics—which states that: 'The entropy of a

system at absolute zero is a universal constant, which may be taken to be zero'. At absolute zero ( $T = 0$  K) the system will be in its ground state. If this is unique,  $\Omega = 1$  and the system is sure to be found in the state. Complete order, therefore, will prevail and  $S$  will be zero.

If  $\Omega = 1$ , every system in the ensemble has got to be in one and the same state. We shall then say that the ensemble is in a *pure* state. If  $\Omega > 1$ , complete specification of the systems is not known and the system is said to be in a *mixed* state.

If the ensemble is in the pure state, in the energy representation, there is only one diagonal element  $\rho_{nn}$  and that is equal to 1, all other elements being zero. The matrix, therefore, satisfies the condition

$$\rho^2 = \rho \quad \dots(7.26)$$

In any other representation

$$\rho_{mn} = \frac{1}{N} \sum_{\alpha=1}^N C_n^{\alpha*}(t) C_m^*(t) = \overline{C_n^*(t) C_m(t)}$$

$$\begin{aligned} \text{Therefore } \rho_{mn}^2 &= \sum_l \rho_{ml} \rho_{ln} = \sum_l \overline{C_l^*(t) C_m(t)} \cdot \overline{C_n^*(t) C_l(t)} \\ &= \overline{C_n^*(t) C_m(t)} = \rho_{mn} \end{aligned} \quad \dots(7.27)$$

Therefore  $\rho^2 = \rho$  is a necessary requirement for a pure state.

(ii) **The canonical ensemble.** In this ensemble  $N$  and  $V$  are fixed and  $E$  is a variable quantity. The most general considerations outlined for classical statistics in Ch. 5 are also valid in quantum statistics. Thus, the probability that a system possesses an energy  $E_n$  is given by

$$P_n = e^{-\beta E_n}$$

Therefore, the density matrix in the energy representation is taken as

$$\rho_{mn} = \rho_n \delta_{mn} \quad \dots(7.28)$$

$$\text{Since, } \text{trace } (\hat{\rho}) = 1, \sum_n e^{-\beta E_n} = 1$$

$$\text{Therefore } C = \frac{1}{\sum_n e^{-\beta E_n}} = \frac{1}{Z(\beta)} \text{ and } \rho_n = \frac{e^{-\beta E_n}}{Z(\beta)} \quad \dots(7.29)$$

where  $Z(\beta) = \sum_n e^{-\beta E_n} = \text{trace } (e^{-\beta \hat{H}})$  is, as before, the partition function of the system. Summation here is over the states and not over the energy eigenvalues.  $\hat{H}$  is the Hamiltonian operator.

The density operator in this ensemble is

$$\hat{\rho} = \sum_n |\phi_n\rangle \frac{e^{-\beta E_n}}{Z(\beta)} \langle \phi_n |$$

$$= \frac{e^{-\beta \hat{H}}}{Z(\beta)} \sum_n |\phi_n\rangle \langle \phi_n|$$

$$= \frac{1}{Z(\beta)} e^{-\beta \hat{H}}$$

The ensemble average of a physical quantity  $G$  is given by

$$\langle \bar{G} \rangle = \text{Tr}(\hat{\rho} \hat{G}) = \frac{\text{Tr}(G e^{-\beta \hat{H}})}{\text{Tr}(e^{-\beta \hat{H}})} \quad \dots(7.30)$$

The other thermodynamic variables are given by

$$\langle \bar{E} \rangle = \text{Trace}(\hat{\rho} \hat{H})$$

$$F = -kT \ln(\text{Tr } e^{-\beta \hat{H}})$$

**Example 7.1** A beam of photons with various polarizations travels along the  $z$ -axis. Determine the probability that the photon is found with polarization along (i)  $x$ -axis, (ii)  $y$ -axis.

Let the state of polarization in the  $x$ -direction be represented by

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ and the state with polarization in the } y\text{-direction by } |\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Therefore the state with an angle  $\varphi$  with the  $x$ -axis is given by

$$\begin{aligned} |\Psi\rangle &= e^{i\alpha} [\cos \varphi |\alpha\rangle + \sin \varphi |\beta\rangle] \\ &= e^{i\alpha} \left[ \cos \varphi \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sin \varphi \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right] \end{aligned}$$

where  $\alpha$  is an overall phase factor.

It can easily be shown that the density matrix in the pure state is

$$\hat{\rho} = \begin{pmatrix} \cos \varphi \\ \sin \varphi \end{pmatrix} (\cos \varphi, \sin \varphi) = \begin{pmatrix} \cos^2 \varphi & \sin \varphi \cos \varphi \\ \sin \varphi \cos \varphi & \sin^2 \varphi \end{pmatrix}$$

Therefore the probability of finding the photon polarized in the  $x$ -direction is

$$\langle \alpha | \hat{\rho} | \alpha \rangle = \cos^2 \varphi$$

The probability for polarization in the  $y$ -direction is  $\sin^2 \varphi$ .

**(iii) The grand canonical ensemble.** In this ensemble both  $N$  and  $E$  are variables. By a generalization of the preceding case, we can write the density operator as

$$\hat{\rho} = \frac{1}{Z(\beta, \mu)} e^{-\beta(\hat{H} - \mu \hat{n})} \quad \dots(7.31)$$

where  $\mu$  is the chemical potential,  $\hat{n}$  is a number operator with eigenvalues 0, 1, 2, ... and  $Z$  is the grand partition function given by

$$\begin{aligned} Z(\beta, \mu) &= \sum_r e^{-\beta(E_r - \mu N_r)} \\ &= Tr \left\{ e^{-\beta(\hat{H} - \mu \hat{n})} \right\} \end{aligned} \quad \dots(7.32)$$

The ensemble average of  $G$  in the grand canonical ensemble is given by

$$\begin{aligned} \langle \bar{G} \rangle &= Tr(\hat{\rho} \hat{G}) \\ &= \frac{Tr \left\{ \hat{G} e^{-\beta(\hat{H} - \mu \hat{n})} \right\}}{Tr \left\{ e^{-\beta(\hat{H} - \mu \hat{n})} \right\}} \end{aligned} \quad \dots(7.33)$$

## PROBLEMS

7.1 Prove, in quantum statistical mechanics that

$$\langle E^2 \rangle - \langle E \rangle^2 = kT^2 C_V$$

7.2 An electron possesses an intrinsic spin  $\frac{1}{2}\hbar\hat{\sigma}$  and a magnetic moment  $\mu_B$ ,  $\sigma$  being the Pauli spin operator. Evaluate the density matrix of an electron spin placed in a magnetic field  $B$ , in the representation that makes  $\hat{\sigma}_z$  diagonal.

Hence show that

$$\langle \sigma_z \rangle = \tanh(\beta \mu_B B)$$

7.3 Evaluate the density matrix of the electron spin in Prob 7.2 above in the representation which makes  $\hat{\sigma}_x$  diagonal. Further, show that the value of  $\langle \hat{\sigma}_x \rangle$  resulting from this representation is the same as that obtained in Prob. 7.2.

**Hint:** Carry out the transformation with the help of unitary

operator 
$$\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{-1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix}$$

7.4 Derive the canonical density matrix ( $\hat{\rho}$ ) for a free particle in a box, in the coordinate representation. Hence, obtain the expectation value of the Hamiltonian  $\hat{H}$ .



# BOSE-EINSTEIN AND FERMI-DIRAC DISTRIBUTION

## 8.1 SYMMETRY OF WAVE FUNCTIONS

Suppose that an enclosure contains a single particle. Let us refer to this particle as particle  $a$ . If the particle is in the  $n$ th state, it will be characterized by a wave function  $\psi_n^a$  determined by the Schrödinger equation

$$H\psi_n^a = E_n^a \psi_n^a \quad \dots(8.1)$$

adopted to the particular boundary conditions of the problem. The energy associated with it is the corresponding eigenvalue  $E_n^a$ . If instead of the particle  $a$ , we were dealing with a particle  $b$  in the  $k$ th state, its wave function would be represented by  $\psi_k^b$  and its energy by  $E_k^b$ .

If both the particles are present simultaneously and they do not interact, this situation is represented by the eigenfunction

$$\psi_n^a \psi_k^b \quad \dots(8.2)$$

and the energy value of the system is  $E_n^a + E_k^b$ .

Let us now exchange the two particles so that  $a$  is in state  $k$  and  $b$  in state  $n$ . The corresponding wave function is

$$\psi_n^b \psi_k^a \quad \dots(8.3)$$

and the corresponding energy  $E_n^a + E_k^a$ . Since the particles are indistinguishable

$$E_n^a + E_k^b = E_n^b + E_k^a \quad \dots(8.4)$$

However  $\psi_n^b \psi_k^a$  is not the same as  $\psi_n^a \psi_k^b$ . Since both situations have the same energy but different wave functions, the system is degenerate. The most general wave function is obtained by taking a linear combination of these wave functions.

Two combinations are particularly simple

$$(i) \quad \psi_n^a \psi_k^b + \psi_n^b \psi_k^a \quad \text{symmetric} \quad \dots(8.5)$$

$$\text{and } (ii) \quad \psi_n^a \psi_k^b - \psi_n^b \psi_k^a,$$

which can be written as a determinant, as

$$\begin{vmatrix} \psi_n^a & \psi_n^b \\ \psi_k^a & \psi_k^b \end{vmatrix} \quad \text{anti-symmetric} \quad \dots(8.6)$$

If  $a$  and  $b$  are interchanged, (i) remains unchanged and for this reason it is called *symmetric* wave function. The same exchange in (ii) leaves the absolute value of the function unaffected but reverses its sign. This function is said to be *anti-symmetric*. It may be noted that Eq. (8.2) and (8.3) are neither symmetric nor anti-symmetric, since, interchanging  $a$  and  $b$ , one is transformed into the other.

Next, suppose that there are  $N$  particles  $a_1, a_2, \dots, a_N$  and that  $a_1$  is in state  $n_1, a_2$  in state  $n_2$ , and so on. The wave function which corresponds to this distribution will be

$$\psi_{n_1}^{a_1} \psi_{n_2}^{a_2}, \dots, \psi_{n_N}^{a_N} \quad \dots(8.7)$$

Any interchange in the distribution of  $N$  particles among  $N$  states entails a change in the wave function. Since the total number of different distributions, with one particle in each state, is  $N!$ , there will be  $N!$  different wave functions of the type (8.7). These are neither symmetric nor anti-symmetric.

Among the linear combinations that may be constructed, the following two obtained by adding  $N!$  fundamental ones are very important:

$$(i) \quad \sum \psi_{n_1}^{a_1} \psi_{n_2}^{a_2}, \dots, \psi_{n_N}^{a_N} \quad \text{symmetric} \quad \dots(8.8)$$

and

$$(ii) \quad \begin{vmatrix} \psi_{n_1}^{a_1} & \psi_{n_2}^{a_2} & \dots & \psi_{n_1}^{a_N} \\ \psi_{n_2}^{a_1} & \psi_{n_2}^{a_2} & & \psi_{n_2}^{a_N} \\ \vdots & & & \\ \psi_{n_N}^{a_1} & \psi_{n_N}^{a_2} & \dots & \psi_{n_N}^{a_N} \end{vmatrix} \quad \text{anti-symmetric} \quad \dots(8.9)$$

The wave functions will be normalized if we multiply them by  $\frac{1}{\sqrt{N!}}$ .

Now, a wave function determines a microscopic state of the system. Different types of wave functions, therefore, will lead us to the different conceptions of the microscopic states, and thereby, as will be shown

presently, to different statistics. Let us examine Eqs. (8.7), (8.8) and (8.9) from this point of view.

Consider a particular case in which the particles  $a_1, a_2, a_3, a_4, a_5$  are in the state  $n_1$  and the remaining  $(N - 5)$  particles in the state  $n_N$ . The wave function of the type (8.7) corresponding to this distribution is

$$\psi_{n_1}^{a_1} \psi_{n_1}^{a_2} \psi_{n_1}^{a_3} \psi_{n_1}^{a_4} \psi_{n_1}^{a_5} \psi_{n_N}^{a_6} \dots \psi_{n_N}^{a_N} \quad \dots(8.10)$$

All other wave functions corresponding to five particles in the state  $n_1$ , and  $N - 5$  in the state  $n_N$ , can be obtained by carrying out all the possible permutations of  $a_1, a_2, \dots, a_N$  in Eq. (8.10). These permutations, however, will not always yield different wave functions. For example, if in Eq. (8.10),  $a_1, a_2, a_3, a_4, a_5$  are permuted among themselves, or if  $a_6 \dots a_N$  are permuted among themselves, the wave function remains unchanged. A permutation will yield a different wave function only if the particles belonging to the different states  $n_1$  and  $n_N$  are interchanged. The total number of distinct wave functions corresponding to five particles in the state  $n_1$  and  $(N - 5)$  in state  $n_N$  is

$$\frac{N!}{5!(N-5)!} \quad \dots(8.11)$$

The probability that five particles are in the state  $n_1$  and  $N - 5$  in the state  $n_N$  is, evidently, proportional to the number (8.11). In other words, (8.11) defines the probability of the corresponding macroscopic states. Recalling the arguments presented in Ch. 5, we see, that the statistics resulting from the selection of wave functions of the type (8.7) is Maxwell-Boltzmann (MB) statistics.

Next, we consider a symmetric function (8.8). If we exchange any two particles, the wave function remains unaffected. Since the interchanging of particles does not generate a new wave function and, hence a new microscopic state, we conclude that when the distribution is described by the wave functions of the type (8.8), the particles cannot be differentiated and do not possess any individuality.

This also hold for the anti-symmetric wave functions. When we exchange particles  $a_1$  and  $a_2$ , we are exchanging two columns of the determinant which remains unaffected by this change, except that its sign is reversed. The change, therefore, does not modify the nature of the wave function and, hence, does not generate a new microscopic state. The interchange of particles in this case too is meaningless. Nevertheless (8.8) and (8.9) have their own peculiarities which we will now consider.

Suppose that all the particles are situated in the state  $n_1$ . The symmetric function describing this distribution is evidently a new one, given by

$$\psi_{n_1}^{a_1} \psi_{n_1}^{a_2} \dots \psi_{n_1}^{a_N} \quad \dots(8.12)$$

However, since the wave function does not vanish, we conclude that such a situation is possible, i.e. we can accommodate any number of

particles in any one state. If the same procedure is followed with the anti-symmetric function (8.9), all the rows of the determinant become identical, and the determinant (and the wave function) vanishes, indicating that such a situation is not possible. Hence, in this case, all the particles cannot be in the same state. In fact, no state can have more than one particle. Because, if we assume two particles in the same state, two rows of the determinant will be identical and the determinant will vanish.

Particles satisfying the symmetry requirement

$$\psi(\dots Q_1 \dots Q_k) = \psi(\dots Q_k \dots Q_1) \quad \dots(8.13)$$

are said to obey Bose-Einstein (BE) statistics and are called bosons, while those satisfying anti-symmetry requirement

$$\psi(\dots Q_1 \dots Q_k) = -\psi(\dots Q_k \dots Q_1) \quad \dots(8.14)$$

are said to obey Fermi-Dirac (FD) statistics and are called fermions. It is known from quantum mechanics that particles having total spin angular momentum which is integral, i.e. 0, 1, 2, ... (ex.  ${}^4\text{He}$ , photons) obey Bose statistics, while those with total spin angular momentum which is half integral, i.e.  $\frac{1}{2}, \frac{3}{2}, \dots$  (electrons), obey Fermi statistics, the most significant

result of which is Pauli's exclusion principle. These findings are summarized in the table given below:

<i>Particle spin</i>	<i>Symmetry of wave function</i>	<i>Statistics</i>	<i>Occupation number</i>
Half-integer	Anti-symmetric	Fermi-Dirac	$n_s = 0, 1$
Integer	Symmetric	Bose-Einstein	$n_s = 0, 1, 2 \dots$

It must be emphasized that when we talk about MB, BE, or FD statistics we are not really referring to different statistics, but only to different distributions.

The following illustration was given by Schrödinger\* to explain the 'new statistics' and its relation to the classical statistics, to those 'who have never heard about such things'. The illustration may seem childishly simple, but is completely adequate and covers the actual situation.

Three schoolboys, Tom, Dick and Harry, deserve a reward. The teacher has two rewards to distribute among them. Before doing so, he wishes to realize for himself how many different distributions are possible. To count the number of different distributions is a statistical question. The answer depends on the nature of the reward. Three different kinds of reward will illustrate the three kinds of statistics.

- (a) The two rewards are two memorial coins with portraits of Newton and Shakespeare, respectively.

The teacher may give Newton to either of Tom, Dick or Harry, and Shakespeare to either of Tom, Dick or Harry. The possible distributions are given in Table S.1

\* E. Schrödinger, *Endeavour* 109, IX, 1950.

Table 8.1

<i>Tom</i>	<i>Dick</i>	<i>Harry</i>
<i>N, S</i>	-	-
<i>N</i>	<i>S</i>	-
<i>N</i>	-	<i>S</i>
<i>S</i>	<i>N</i>	-
-	<i>N, S</i>	-
-	<i>N</i>	<i>S</i>
-	<i>S</i>	<i>N</i>
<i>S</i>	-	<i>N</i>
-	-	<i>N, S</i>

Thus, there are  $3 \times 3 = 9$  different distributions.

(b) The two rewards are two-shilling pieces:

Either Tom, Dick or Harry receives two shillings or they can be given to two different boys, the third going without.

<i>Tom</i>	<i>Dick</i>	<i>Harry</i>
2	-	-
-	2	-
-	-	2
1	1	-
1	-	1
-	1	1

Thus, the total number of distributions is 6.

(c) The two rewards are two vacancies in the football team:

In this case, two boys can join the team, and one of the three is left out.

<i>Tom</i>	<i>Dick</i>	<i>Harry</i>
*	*	-
*	-	*
-	*	*

Thus there are three different distributions.

Now let the rewards represent the particles, and the boys represent states the particles can assume. In the first case the particles are distinguishable and so obey MB statistics. Shillings are not distinguishable but they are capable of being owned in the plural. It makes a difference whether one has one shilling or two. There is no point in the two boys exchanging their shillings. The situation corresponds to Bose-Einstein statistics. With memberships, neither has a meaning. You can either belong to a team or not. You cannot belong to it twice over. The third

case, therefore, corresponds to Fermi-Dirac statistics, in which there can be only one particle in a state.

It would be interesting to find how the ratio  $r$  of the probability that the two particles are found in the same state to the probability that they belong to different states, varies in the three cases.

We find that

$$r_{MB} = \frac{3}{6} = \frac{1}{2}$$

$$r_{BE} = \frac{3}{3} = 1$$

$$r_{FD} = \frac{0}{3} = 0$$

Thus, in the BE statistics there is a greater tendency for particles to crowd in the same state than in classical statistics, while in FD statistics the tendency is to remain apart.

## 8.2 THE QUANTUM DISTRIBUTION FUNCTIONS

Consider an ideal gas of identical particles,  $N$  in number. Let  $s$  represent the state of a single particle and  $S$  the state of the whole gas. Suppose that when the gas is in state  $S$ ,  $n_1$  particles are in state  $s = 1$  with energy  $\epsilon_1$ ,  $n_2$  particles in state  $s = 2$  with energy  $\epsilon_2$ , etc. The total energy of the gas, therefore, is

$$E_S = \sum_s n_s \epsilon_s \quad \dots(8.15)$$

and the total number of particles

$$N = \sum_s n_s \quad \dots(8.16)$$

The physical quantities, we are interested in, can be calculated with the help of the partition function

$$Z = \sum_S e^{-\beta E_S}$$

summation here being over all possible states  $S$ . While summing over the states we have to take note of what type of statistics the particles obey.

(i) **MB Statistics:** In this case the particles are distinguishable. The partition function is

$$Z = \sum_S e^{-\beta \sum_s n_s \epsilon_s} \quad \dots(8.17)$$

where the summation is over all states  $S$ , i.e. over all possible values of  $n_s$ .

The mean number of particles in state  $s$

$$\langle n_s \rangle = \frac{\sum_s n_s e^{-\beta \sum_s n_s \epsilon_s}}{\sum_s e^{-\beta \sum_s n_s \epsilon_s}} \quad \dots(8.18)$$

$$= -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} \quad \dots(8.19)$$

The partition function can as well as written as

$$Z = \sum_s e^{-\beta(\epsilon_{s_1} + \epsilon_{s_2} + \dots + \epsilon_{s_n})} \quad \dots(8.20)$$

where the summation is over all the possible states of each individual particles  $s_1, s_2$ , etc. One can see that the summation carried out in this manner takes into account the distinguishability of the particles:

$$\begin{aligned} Z &= \sum_{s_1, s_2} e^{-\beta \epsilon_{s_1}} e^{-\beta \epsilon_{s_2}} \dots \\ &= \left[ \sum_{s_1} e^{-\beta \epsilon_{s_1}} \right] \left[ \sum_{s_2} e^{-\beta \epsilon_{s_2}} \right] \dots \\ &= \left[ \sum_{s_1} e^{-\beta \epsilon_{s_1}} \right]^N \end{aligned} \quad \dots(8.21)$$

and

$$\ln Z = N \ln \left( \sum_s e^{-\beta \epsilon_{s_1}} \right) \quad \dots(8.22)$$

Therefore, substituting this in Eq. (8.19), we have

$$\langle n_s \rangle = \frac{N e^{-\beta \epsilon_s}}{\sum_s e^{-\beta \epsilon_s}} \quad \dots(8.23)$$

which is the MB distribution obtained previously in classical statistical mechanics.

**(ii) BE Statistics:** In this case the particles are indistinguishable. BE and FD statistics can be treated conveniently using the grand canonical ensemble as  $N$  also is involved.

The grand partition function is given by

$$Z = \sum_S e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots) + \mu \beta(n_1 + n_2 \dots)} \quad \dots(8.24)$$

where the summation is over all possible states, i.e. over all possible numbers of particles in each single particle state. The number of particles  $n_i$  in each state  $i$ , will be 0, 1, 2, ..., subject to the condition  $\sum n_i = N$

Therefore  $Z = \left( \sum_{n_1} e^{-\beta(\epsilon_1 - \mu)n_1} \right) \left( \sum_{n_2} e^{-\beta(\epsilon_2 - \mu)n_2} \right) \dots$

Now  $\sum_{n_1} e^{-\beta(\epsilon_1 - \mu)n_1} = 1 + e^{-\beta(\epsilon_1 - \mu)} + e^{-2\beta(\epsilon_1 - \mu)} + \dots \quad \dots(8.25)$

This is a geometric series. Hence

$$\sum_{n_1} e^{-\beta(\epsilon_1 - \mu)n_1} = \frac{1}{1 - e^{-\beta(\epsilon_1 - \mu)}}$$

Therefore  $Z = \left( \frac{1}{1 - e^{-\beta(\epsilon_1 - \mu)}} \right) \left( \frac{1}{1 - e^{-\beta(\epsilon_2 - \mu)}} \right) \dots \quad \dots(8.26)$

and  $\ln Z = -\sum_s \ln \left( 1 - e^{-\beta(\epsilon_s - \mu)} \right) \quad \dots(8.27)$

We know that  $N = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu}$  (see Prob 6.3)

therefore  $N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \sum_s \ln \left\{ 1 - e^{-\beta(\epsilon_s - \mu)} \right\} = \sum_s \langle n_s \rangle$

From this expression one can infer that the  $s$ th term in the sum represents the average number of molecules in the  $s$ th level.

$$\langle n_s \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \left\{ 1 - e^{-\beta(\epsilon_s - \mu)} \right\} \quad \dots(8.28)$$

$$= \frac{e^{-\beta(\epsilon_s - \mu)}}{1 - e^{-\beta(\epsilon_s - \mu)}} = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1} = f(\epsilon_s) \quad \dots(8.29)$$

Since the number of bosons in any state cannot be negative,  $e^{\beta(\epsilon_s - \mu)}$  must be greater than unity, i.e.  $(\epsilon_s - \mu) > 0$  for all  $\epsilon_s$ . The lowest energy of a single particle state of a boson gas is zero. Hence,  $\mu$  for an ideal boson gas always be negative.

The formula (8.29) takes a simpler form in the case of photons, which have spin one and, hence, are bosons. Photons can be considered as an ideal gas, since it follows from electromagnetic theory that their interactions are completely negligible. Because photons may be absorbed and re-emitted by the walls of the enclosure, the number of photons inside the enclosure is not conserved. The conditions  $\sum n_s = N$ , therefore,

is not imposed on the distribution. Hence  $\frac{\partial \ln Z}{\partial N} = 0$ .

Therefore  $\mu = \left( \frac{\partial E}{\partial N} \right)_{V,T} = kT \frac{\partial \ln Z}{\partial N} = 0$

and the distribution function takes the form

$$\langle n_s \rangle = \frac{1}{e^{\beta \epsilon_s} - 1} \quad \dots(8.30)$$

In fact, this formula could have been derived directly. Thus

$$\begin{aligned} Z &= \sum_S e^{-\beta E_s} = \sum_{n_1, n_2, \dots} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \\ &= \left( \sum_{n_1}^{\infty} e^{-\beta n_1 \epsilon_1} \right) \left( \sum_{n_2}^{\infty} e^{-\beta n_2 \epsilon_2} \right) \dots \\ &= \left( \frac{1}{1 - e^{-\beta \epsilon_1}} \right) \left( \frac{1}{1 - e^{-\beta \epsilon_2}} \right) \dots \end{aligned}$$

Therefore  $\ln Z = - \sum_S \ln(1 - e^{-\beta \epsilon_s})$

and  $\langle n_s \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_s} = \frac{1}{e^{\beta \epsilon_s} - 1}$

**(iii) FD Statistics:** For FD systems,  $n_s = 0$  or  $1$

Therefore  $Z = (1 + e^{\beta(\mu - \epsilon_1)}) (1 + e^{\beta(\mu - \epsilon_2)}) \dots$

$$\ln Z = \sum_s \ln \{1 + e^{\beta(\mu - \epsilon_s)}\} \quad \dots(8.31)$$

Hence  $N = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = \sum_s \frac{e^{\beta(\mu - \epsilon_s)}}{1 + e^{\beta(N - \epsilon_s)}} = \sum \langle n_s \rangle$

therefore  $\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu_s)} + 1} \quad \dots(8.32)$

This shows that if  $j\epsilon_s$  is very large  $n_s \rightarrow 0$ , if on the other hand,  $\epsilon_s$  is small, since the denominator is always greater than one, we have

$$\langle n_s \rangle \leq 1 \quad \dots(8.33)$$

The behaviour of the gas obeying FD statistics is different from that obeying BE statistics. This difference becomes particularly striking as  $T$  tends to zero, when the gas is in the state of lowest energy. In the case of BE statistics, since there is no restriction on the number of particles to be placed in any one single particle state, the gas will have the lowest energy state. But in the case of FD statistics, since we can place only one particle in any one single particle state, even though the gas has lowest energy, one is forced to populate the successive states of higher energy with one particle in each. The lowest energy of a gas obeying FD statistics, therefore, is much higher than that it would have been if the particles had obeyed BE statistics.

### 8.3 THE BOLTZMANN LIMIT OF BOSON AND FERMION GASES

We have seen that the mean occupation number of particles in any energy state  $\epsilon_s$  is given by

$$\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)} \pm 1} \quad \dots(8.34)$$

where the upper sign refers to FD statistics and the lower to BE statistics.  
Suppose now

$$e^{-\beta\mu} \gg 1 \quad \text{i.e. } e^{\beta(\epsilon_s - \mu)} \gg 1 \quad \dots(8.35)$$

In this case  $\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)}} = e^{\beta\mu} e^{-\beta\epsilon_s}$

Further, because  $\sum \langle n_s \rangle = N$

$$e^{\beta\mu} \sum_s e^{-\beta\epsilon_s} = N$$

Therefore  $e^{\beta\mu} = \frac{N}{\sum e^{-\beta\epsilon_s}}$

and, hence  $\langle n_s \rangle = \frac{Ne^{-\beta\epsilon_s}}{\sum e^{-\beta\epsilon_s}}$

which is MB distribution.

Thus, quantum statistics given the Boltzmann form in the limiting case when

$$e^{-\beta\mu} \gg 1 \quad \dots(8.36)$$

i.e.  $\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \left(\frac{V}{N}\right) \gg 1$  [see Eq. (6.95)]  $\dots(8.37)$

This condition is satisfied if  $T$  is high and  $N/V = \rho$  very low.

This variation of the occupation number  $\langle n_s \rangle$  with  $\beta(\epsilon - \mu)$  in the three cases is shown in Fig. 8.1.

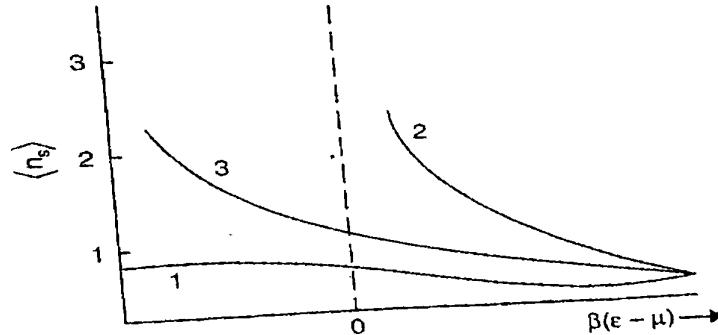


Fig. 8.1

Curve 1 is for fermions, 2 for bosons and 3 for MB particles. We find, that for large values of  $\beta(\epsilon - \mu)$  the quantum curves 1 and 2 merge into the classical curve 3. We know that the classical treatment is valid at high temperatures. Therefore, at high  $T$ , if  $\frac{\epsilon - \mu}{kT}$  is to be high,  $\mu$  must be negative and large in magnitude, the result arrived at the Eq. (8.36). Thus, for classical treatment to be valid

$$\frac{1}{\lambda_T^3} \left( \frac{V}{N} \right) \gg 1 \text{ or } \left( \frac{N\lambda_T^3}{V} \right) \ll 1 \text{ [see Eq. (8.37)]} \quad \dots(8.38)$$

where we have introduced the mean thermal wavelength

$$\lambda_T = \frac{h}{(2\pi mkT)^{1/2}} \quad \dots(8.39)$$

The thermal wavelength is a measure of the wave function of the particles. As long as  $\lambda_T$  is much smaller than the average particle spacing, statistics will be classical.

A gas which can be treated classically is said to be non-degenerate. On the other hand, if quantum statistical distributions are to be used, the gas is said to be degenerate. We can see from Eq. (8.37) that when

$$\left( \frac{h^2}{2\pi mkT} \right)^{3/2} \left( \frac{N}{V} \right) \gg 1 \quad \dots(8.40)$$

the gas is degenerate. The condition (8.40) is known as *degeneracy criterion*.

**Example 8.1** Determine whether the electron gas in copper at room temperature is degenerate or non-degenerate. (Concentration of electrons in copper is  $8.5 \times 10^{28} \text{ m}^{-3}$ ).

From Eq. (8.40), we get

$$\begin{aligned} & \left( \frac{h^2}{2\pi mkT} \right)^{3/2} \left( \frac{N}{V} \right) \\ &= \frac{(6.62 \times 10^{-34})^{3/2}}{(2\pi \times 9.10^{-31} \times 1.38 \times 10^{-23} \times 300)^{3/2}} \times 8.5 \times 10^{28} \\ &= 6775 (>>1) \end{aligned}$$

Therefore the gas is degenerate.

## 8.4 EVALUATION OF THE PARTITION FUNCTION

Consider an ideal gas, consisting of a large number of molecules  $N$  enclosed in a volume  $V$ . In addition to the translational motion, the molecules may

have rotational and vibrational motion, or they may get electronically excited.

If, as a first approximation, we assume that the molecules have no mutual intermolecular forces, the total energy of the molecules is given by

$$E_{\text{mol}} = E_{\text{trans}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{rot}} \quad \dots(8.41)$$

and the canonical partition function of the molecule will be

$$Z = Z_{\text{trans}} \cdot Z_{\text{rot}} \cdot Z_{\text{vib}} \cdot Z_{\text{el}}$$

Consider first a monatomic gas. Since it does not have any rotational or vibrational motion

$$E_{\text{mol}} = E_{\text{trans}} + E_{\text{el}}$$

Let us first calculate the translational partition function.

Without loss of generality, we can assume the enclosure to be in the shape of a rectangular parallelepiped with edge lengths  $L_x, L_y, L_z$  in the directions  $x, y, z$ , respectively.

Therefore  $V = L_x, L_y, L_z$

We know from quantum mechanics that possible quantized energies are given by

$$\begin{aligned} \epsilon &= \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \\ &= \frac{2\pi\hbar^2}{m} \left( \frac{n_x^2}{L_x^2} = \frac{n_y^2}{L_y^2} = \frac{n_z^2}{L_z^2} \right) \end{aligned} \quad \dots(8.42)$$

The partition function is

$$\sum_s e^{-\beta \epsilon_s}$$

but in this, the energy levels being closely spaced, the quantization of the translational levels can be neglected, and summation may safely be replaced by integration. The notion of phase space is not used in quantum mechanics in the same context as it is used in classical mechanics, for, the principle of indeterminacy makes it impossible to simultaneously specify the coordinate and the conjugate momentum of the particle. To be able to make a transition from a sum over discrete states to an integral over continuous states, one needs to know what volume in phase space corresponds to a discrete quantum state. Since it is impossible to define the position of a representative point in the phase space more accurately than allowed by the condition  $\Delta p \Delta q \approx h$ , we assume that a discrete quantum state occupies a volume equal to  $h^{3N}$ , where  $h$  is Planck's constant and  $3N$  the number of degrees of freedom. In fact, this can be easily proved in the case of a particle moving freely within a cube of edge  $L$  (Prob 8.1). In a volume element  $d^3q d^3p$  in  $\mu$ -space, therefore, there are  $(1/h^3) d^3q d^3p$  possible states. So the summation over all energy states can be replaced by an integration of the differential

$$\frac{1}{h^3} e^{-\beta \epsilon_s} d^3 q d^3 p$$

Therefore  $Z_1 = \frac{1}{h^3} \int \dots \int e^{-\beta p_2^2 m} d^3 q d^3 p$  ... (8.43)

Integration over  $d^3 q$  gives the volume of the container  $V$ .

Therefore  $Z_1 = \frac{V}{h^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)} dp_x dp_y dp_z$

$$= \frac{V}{h^3} (2\pi m k T)^{3/2}$$
 ... (8.44)

Thus the correct partition function is

$$Z = Z_1^N = \frac{V^N}{h^{3N}} (2\pi m k T)^{3N/2}$$
 ... (8.45)

This result is the same as obtained classically, except that the arbitrary parameter  $h_0$ , measuring the size of the cell in classical phase space, is replaced by Planck's constant  $h$ . The expressions for the thermodynamic quantities  $S$ ,  $\langle F \rangle$ ,  $\langle P \rangle$ , etc. are the same as those, calculated in Ch. 6 except that  $\sigma_0$  has now a definite value in terms of  $h$ .

## 8.5 PARTITION FUNCTION FOR DIATOMIC MOLECULES

### (a) Translational Partition Function

The translational motion of a diatomic molecules is analogous to that already considered for a structureless molecule and the partition function will be the same as given by Eq. (8.45) with  $m$  replaced by  $m_1 + m_2$ ,  $m_1$ ,  $m_2$  being the masses of the two atoms.

Therefore  $Z_1 = \frac{V}{h^3} [2\pi(m_1 + m_2)kT]^{3/2}$  ... (8.46)

### (b) Rotational Partition Function

To a first approximation, the molecule may be visualized as a pair of masses  $m_1$ ,  $m_2$  separated by a fixed distance  $r_0$ .

The energy levels of such a rotator is given by

$$\epsilon_{rot} = \frac{\hbar^2}{2I_m} J(J+1)$$
 ... (8.47)

where  $J$  is the rotational quantum number and takes values 0, 1, 2, ....

and  $I_m = \mu r_0^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2$  is the moment of inertia of the molecule.

Since  $(2J + 1)$  is the degeneracy of the  $J$ th state (i.e., for a given  $J$ , there are  $2J + 1$  possible quantum states of the same energy)

$$Z_{rot} = \sum_{j=0}^{\infty} (2J + 1) e^{-\beta(\hbar^2/2I_m)J(J+1)} \quad \dots(8.48)$$

$$= \sum_{j=0}^{\infty} (2J + 1) e^{-\frac{\theta_r}{T}J(J+1)} \quad \dots(8.49)$$

where  $\theta_r = \hbar^2/2kI_m$  is called the rotational characteristic temperature.

Consider the following cases:

(i)  $T$  or  $I_m$  very small

$$Z_{rot} = 1 + 3e^{-\theta_r/T} + 5e^{-6\theta_r/T} + \dots \quad \dots(8.50)$$

In the low temperature region, because the thermal energy of the order of  $kT$  is not enough to populate the higher rotational levels, almost all molecules will be in the lowest rotational state and, hence, all terms beyond the first few are negligible.

(ii)  $T$  is reasonably high and  $I_m$  not small. In this case the spacing between the consecutive levels is very small compared to  $kT$ , and hence,  $\epsilon$  may be considered as a continuous variable in  $J$  and summation can be replaced by integration. Put  $u = J(J + 1)$

$$\text{Therefore } Z_{rot} = \int_0^{\infty} e^{-\beta u^2/2I_m} du = \frac{2I_m}{\beta \hbar^2} = \frac{2I_m kT}{\hbar^2} \quad \dots(8.51)$$

(iii) Homonuclear molecules: Consider first the case when the temperature is so high that the classical approximation discussed in (ii) above is admissible. If the two nuclei are identical, the two opposing positions of the molecular axis, viz. those that correspond to the azimuthal angles  $\phi$  and  $\phi + \pi$  correspond to only one discrete state of the molecule, because they differ simply by an interchange of the two identical nuclei. The partition function given by Eq. (8.51), therefore, will be reduced by a factor of 2. Thus in the classical approximation

$$Z_{rot} = \frac{2I_m kT}{2\hbar^2} \quad \dots(8.52)$$

The general formula for the rotational partition function is

$$Z_{rot} = \frac{2I_m kT}{\sigma \hbar^3} \quad \dots(8.53)$$

where the number  $\sigma$  is

$$\sigma = \begin{cases} 1 & \text{for heteronuclear molecules} \\ 2 & \text{for diatomic molecules} \\ 3 & \text{for molecules with 3-fold symmetry} \end{cases}$$

$$\text{Since } \langle E \rangle = -N \frac{\partial \ln Z}{\partial \beta} = NkT \quad \dots(8.54)$$

the contribution of rotational energy to the specific heat is

$$C_{V(rot)} = Nk \quad \dots(8.55)$$

(iv) At lower temperature, the rotational states have to be treated as discrete, in which case the rotational partition function is given by Eq. (8.49), viz.

$$Z_{rot} = \sum_j (2J+1) e^{-J(J+1)\theta_r/T}$$

The heat capacities calculated from this formula, however, do not generally agree with those obtained experimentally. This discrepancy is resolved if the symmetry character of the nuclear wave function is taken into consideration.

Consider, for example, a  $H_2$  molecule. Both nuclei are identical, each having a spin  $1/2$ . The total spin of the pair can either be 0 or 1. In the former case the molecules are in a single *t* state (*para* hydrogen) and in the latter, they are in the triplet state (*ortho* hydrogen), their statistical weights ( $2I + 1$ ) being 1 and 3, respectively. Pauli principle demands that the total wave function must be anti-symmetric with respect to the exchange of the two nuclei. The electronic and vibrational wave functions are symmetric in the ground state. The rotational wave function is symmetric for even values of  $J$  and anti-symmetric for odd values. Since the nuclear spin function for *ortho* hydrogen is symmetric under the exchange of the nuclei, the rotational part of the wave function must be anti-symmetric.

$$\text{Therefore } Z_0 = \sum_{\text{odd } J} e^{-J(J+1)\theta_r/T} \cdot (2J+1) \quad \dots(8.56)$$

For *para* hydrogen, since the nuclear spin function is anti-symmetric, the rotational partition function is

$$Z_p = \sum_{\text{even } J} e^{-J(J+1)\theta_r/T} \cdot (2J+1) \quad \dots(8.57)$$

The total partition function per molecule, if the system is in thermal equilibrium is

$$Z = 3Z_0 + Z_p \quad \dots(8.58)$$

and, hence, the heat capacity is given by

$$C_v = \frac{3}{4} C_{v(o)} + \frac{1}{4} C_{v(p)} \quad \dots(8.59)$$

This shows a fairly good agreement with the experiment, where *o* and *p* means *ortho* and *para* contributions to the specific heat.

### (c) Vibrational Partition Function

To a good approximation, the vibrational motion of a molecule may be assumed to be simple harmonic in form. Energy of a harmonic oscillator is given by

$$\epsilon_n = \hbar\omega \left( n + \frac{1}{2} \right)$$

Therefore

$$\begin{aligned} Z_{vib} &= \sum_{n=0}^{\infty} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} \\ &= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \end{aligned} \quad \dots(8.60)$$

$$\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = 1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots \quad \dots(8.61)$$

$$= \frac{1}{1 - e^{-\beta\hbar\omega}} \quad \text{a geometric series}$$

$$\text{Therefore } Z_{vib} = e^{-\beta\hbar\omega/2} \frac{1}{1 - e^{-\beta\hbar\omega}} \quad \dots(8.62)$$

$$= e^{-\theta_v/2T} \left[ 1 - e^{-\theta_v/2T} \right]^{-1} \quad \dots(8.63)$$

where  $\theta_v = \hbar\omega/k$  is the *vibrational characteristic temperature*.

$$\begin{aligned} \text{Therefore } \langle E \rangle &= -N \frac{\partial \ln Z}{\partial \beta} = NkT^2 \frac{\partial \ln Z}{\partial T} \\ &= NkT^2 \frac{\partial}{\partial T} \left[ -\frac{\theta_v}{2T} - \ln \left( 1 - e^{-\theta_v/T} \right) \right] \\ &= NkT^2 \left[ \frac{\theta_v}{2T^2} + \frac{e^{-\theta_v/T}}{1 - e^{-\theta_v/T}} \frac{\theta_v}{T^2} \right]. \\ &= Nk \left[ \frac{\theta_v}{2} + \frac{\theta_v}{e^{\theta_v/T} - 1} \right] \end{aligned} \quad \dots(8.64)$$

and

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = Nk \left( \frac{\theta_v}{T} \right)^2 \frac{e^{\theta_v/T}}{\left( e^{\theta_v/T} - 1 \right)^2} \quad \dots(8.65)$$

At high temperatures  $\frac{\theta_v}{T} \ll 1$

$$\text{Therefore } e^{\theta_v/T} \equiv 1 + \frac{\theta_v}{T} + \frac{1}{2} \left( \frac{\theta_v}{T} \right)^2$$

neglecting the higher terms.

Therefore  $\langle E \rangle \approx Nk\theta_v \left[ \frac{1}{2} + \frac{1}{\frac{\theta_v}{T} + \frac{1}{2} \left( \frac{\theta_v}{T} \right)^2} \right]$

$$\equiv N\hbar\omega \left[ \frac{1}{2} + \frac{T}{\theta_v} \left( 1 - \frac{\theta_v}{2T} \right) \right]$$

$$= NkT + N\hbar\omega/2 \quad \dots(8.66)$$

and, hence  $C_v = Nk \quad \dots(8.67)$

#### (d) Electronic Partition Function

The electronic partition function is given by

$$Z_{el} = g_0 + g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} + \dots \quad \dots(8.68)$$

where  $\epsilon_1, \epsilon_2, \dots$  are the energies required for the excitation of the electron, to the various levels and  $g$ 's are the respective degeneracies. The energies  $\epsilon_1, \epsilon_2, \dots$  being generally much larger than the thermal energy  $kT$ , at room temperature the molecules of most of the gases are hardly excited to higher electronic states. The electronic partition function, therefore, can be represented with sufficient accuracy by the first two terms of Eq. (8.68). Thus

$$Z_{el} = g_0 + g_1 e^{-\beta\epsilon_1} \quad \dots(8.69)$$

Therefore  $\langle E \rangle = NkT^2 \frac{g_1 e^{-\beta\epsilon_1}}{(g_0 + g_1 e^{-\beta\epsilon_1})} \cdot \frac{\epsilon_1}{kT^2}$

$$= N\epsilon_1 \left( \frac{g_0}{g_1} e^{\beta\epsilon_1} + 1 \right)^{-1} \quad \dots(8.70)$$

and  $C_v = \frac{N\epsilon_1^2}{kT^2} \frac{g_0}{g_1} e^{\beta\epsilon_1} \left[ 1 + \frac{g_0}{g_1} e^{\beta\epsilon_1} \right]^{-2} \quad \dots(8.71)$

Since there will be no significant contribution from the electronic energy to the specific heat, except at high temperatures, the total temperature dependent energy of the gas is given by

$$E = \frac{3}{2} NkT_{(trans)} + NkT_{(root)} + NkT_{(vib)}$$

$$= \frac{7}{2} NkT \quad \dots(8.72)$$

and the total specific heat

$$C = \frac{7}{2} Nk \quad \dots(8.73)$$

## 8.6 EQUATION OF STATE FOR AN IDEAL GAS

In MB statistics we have seen that

$$PV = NkT \text{ and } E = \frac{3}{2} NkT$$

Therefore  $PV = \frac{2}{3} E$  ... (8.74)

We will now show that the equation of state [Eq. (8.74)] retains its form in quantum statistics too.

We know from Eqs. (8.27) and (8.31) that

$$\ln Z = \sum_s \ln(1 \pm e^{-\beta(\epsilon_s - \mu)})^{\pm 1} \quad \dots (8.75)$$

where the upper sign is for FD statistics and the lower for BE statistics. If  $V$  is very large, the summation can be replaced by integration.

Number of states with momenta between  $p$  and  $p + dp$  is

$$\frac{d^3 q d^3 p}{h^3} = \frac{V}{h^3} d^3 p = \frac{V}{h^3} 4\pi p^2 dp \quad \dots (8.76)$$

Replacing  $p^2$  by  $2m\epsilon$ , the number of states in the energy range  $\epsilon$  and  $\epsilon + d\epsilon$

$$= \frac{4\pi V}{8\pi^3 \hbar^3} 2m\epsilon \frac{\sqrt{2m}}{2\sqrt{\epsilon}} d\epsilon = \frac{V}{4\pi^2 \hbar^2} (2m)^{3/2} \epsilon^{1/2} d\epsilon \quad \dots (8.77)$$

Now  $E = \Sigma \langle n \rangle \epsilon = \int \frac{\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1} \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$

$$= \frac{V(2m)^{3/2}}{4\pi^2 \hbar^2} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1} \quad \dots (8.78)$$

and

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}$$

$$= \frac{1}{\beta} \frac{\partial}{\partial V} \int_0^\infty \ln(1 \pm e^{-\beta(\epsilon-\mu)})^{\pm 1} \frac{V}{4\pi^2 \hbar^2} (2m)^{3/2} \epsilon^{1/2} d\epsilon$$

$$= \frac{(2m)^{3/2}}{4\pi^2 \hbar^3} \int_0^\infty \epsilon^{3/2} \ln(1 \pm e^{-\beta(\epsilon-\mu)})^{\pm 1} d\epsilon$$

$$= \pm \frac{(2m)^{3/2}}{4\pi^2 \hbar^3 \beta} \left[ \frac{2}{3} \epsilon^{3/2} \ln(1 \pm e^{-\beta(\epsilon-\mu)}) \right]_0^\infty$$

$$\mp \frac{(2m)^{3/2}}{4\pi^2 \hbar^3 \beta} \cdot \frac{2}{3} \int_0^\infty \frac{\epsilon^{3/2} \beta(-\mp e^{-\beta(\epsilon-\mu)})}{1 \pm e^{-\beta(\epsilon-\mu)}} d\epsilon$$

the first term vanishes at both the limits. Therefore

$$\begin{aligned} P &= \frac{2}{3} \frac{(2m)^{3/2}}{4\pi^2 \hbar^3} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon - \mu) \pm 1}} d\epsilon \\ &= \frac{2}{3} \frac{E}{V} \end{aligned} \quad \dots(8.79)$$

Therefore

$$PV = \frac{2}{3} E \quad \dots(8.80)$$

Thus the relation  $PV = 2/3 E$  is satisfied by a gas of free monatomic particles, irrespective of the statistics it obeys. The variation of  $E$  with  $T$  at constant volume in the case of BE and FD distribution is shown in Fig.

8.2. The dotted line shows the variation of  $E$  with  $T$  ( $E = \frac{3}{2} NkT$ ) for an

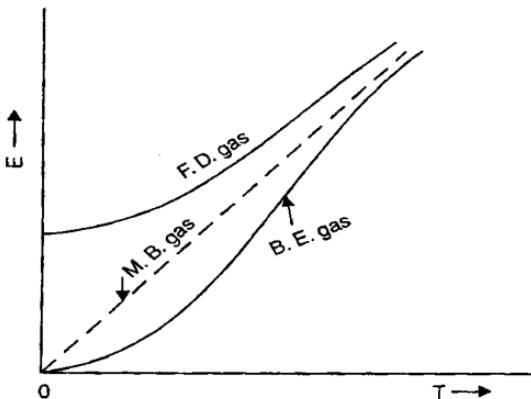


Fig. 8.2

ideal monatomic gas in the classical limit. We can see that the total energy of an ideal boson gas is always less than that of an ideal monatomic classical gas while the energy of FD gas is more than that of the ideal monatomic gas. At higher temperatures the energies of BE and FD gases approach that of the classical gas. From Eq. (8.80) we conclude that the variation of pressure with temperature has the same trend as the variation of energy.

## 8.7 THE QUANTUM MECHANICAL PARAMAGNETIC SUSCEPTIBILITY

We have given the classical treatment of paramagnetism in Ch. 6. In this section we will treat the problem quantum mechanically.

We know that the angular momentum number  $J$  of an atom or a molecule takes discrete values and its component  $M_J$  in the direction of

an applied magnetic field  $B$  can take all values between  $J$  and  $-J$  in integral steps. Thus

$$M_J = -J, -J+1, \dots, J-1, J \quad \dots(8.81)$$

The magnetic moment associated with a given  $M_J$  is

$$\mu = g\mu_B M_J \quad \dots(8.82)$$

where  $g$  is Lande's  $g$ -factor and  $\mu_B$  is the Bohr magneton.

The magnetic potential energy of the molecule is  $-\mu B$ .

Therefore, the partition function  $Z_{mag}$  will be

$$Z_{mag} = \sum e^{\beta \mu B} = \sum_{\mu_J=-J}^J e^{\beta g\mu_B M_J B} \quad \dots(8.83)$$

Suppose  $B$  is very large. In this case all the magnetic moments will be aligned in the direction of the field applied, leading to a state of magnetic saturation, the maximum possible magnetic moment being  $n g \mu_B J$  where  $n$  is the number of atoms per unit volume.

If, on the other hand, the applied field is weak, the exponential function may be expanded in the form of a series. Thus, putting  $x = \beta g \mu_B J$

$$\sum_{M_J=-J}^J e^{x M_J} = \sum_{M_J=-J}^J \left( 1 + x M_J + \frac{x^2}{2!} M_J^2 \right) \quad \dots(8.84)$$

higher terms being neglected.

$$\text{Therefore } \sum_{M_J=-J}^J e^{x M_J} = 2J + 1 + \frac{x^2}{2} \sum_{M_J=-J}^J M_J^2 \quad \dots(8.85)$$

(because  $\sum_{M_J=-J}^J M_J$  vanishes)

$$= 2J + 1 + \frac{x^2}{2} \frac{J(J+1)(2J+1)}{3} \quad \dots(8.86)$$

$$\begin{aligned} \text{Now } E_{mag} &= -\frac{n \partial \ln Z}{\partial \beta} \\ &= -n \frac{\partial}{\partial \beta} \ln \left\{ 2J + 1 + \frac{x^2 J(J+1)(2J+1)}{6} \right\} \\ &= \frac{-n \beta (g \mu_B B)^2 \frac{J(J+1)(2J+1)}{3}}{2J + 1 + \frac{x^2 J(J+1)(2J+1)}{6}} \quad \dots(8.87) \end{aligned}$$

Since  $B$  is very low  $g \mu_B B \ll kT$ .

Therefore  $x \ll 1$  and, hence, the term containing  $x^2$  in the denominator may be neglected.

$$\text{Therefore } E_{\max} = -\frac{ng^2\mu_B J(J+1)}{3kT} B \quad \dots(8.88)$$

The magnetic moment per unit volume

$$m = -\frac{E}{V} = \frac{ng^2\mu_B^2 J(J+1)}{3kT} B \quad \dots(8.89)$$

Hence, the susceptibility per unit volume,  $m/B$ , is

$$\chi = \frac{ng^2\mu_B^2 J(J+1)}{3kT} \quad \dots(8.90)$$

This differs from the expression for  $\chi$  obtained classically in Chapter 6, in that  $g\mu_B\sqrt{J(J+1)}$  takes the place of  $\mu$  in the classical expression.

There is hardly any element for which we can verify the formula (8.89) as applied to the gaseous state. However, it has been possible to verify it in the case of chemical compounds of rare-earth elements, where other elements do not possess a characteristic magnetic moment. In rare-earths the moment of the electronic cloud is due to the  $4f$ -shell, which is deep inside the atom and, hence, is not much affected by the electric field of the neighbouring atoms. Their state, therefore, may be regarded as that of free atoms of a rare-earth element. The agreement of the formula (8.89) with experiment is found to be fairly good.

## PROBLEMS

- 8.1 Considering the free motion of a particle in a cubical box, show that the volume in phase space corresponding to a discrete quantum state is  $\hbar^3$ .
- 8.2 Assuming that only the ground state and the first excited state of a simple harmonic one-dimensional oscillator are appreciably populated, find the mean energy of the oscillator.
- 8.3 Discuss whether the classical treatment would be valid for  ${}^4\text{He}$  gas at
  - (i) NTP
  - (ii) at 3 K and atmospheric pressure.
- 8.4 Find the value of  $Z$  for helium gas at pressure 1 Torr and temperature 300 K.
- 8.5 Show that, when  $T \ll \theta_r$ , where  $\theta_r$  is the rotational characteristic temperature in the lowest approximation

$$(C_v)_{rot} = 12Nk\left(\frac{\theta_r}{T}\right)^2 e^{-\theta_r N/T}$$

- 8.6 The nuclear spin of deuterium ( $D_2$ ) is 1. Find its rotational partition function.

- 8.7 Calculate the contribution of the vibration of molecules to the heat capacity of a diatomic gas consisting of  $N$  molecules at an absolute temperature equal to the characteristic temperature  $Q_v$ .

- 8.8 The following data were obtained from the intensity measurements of the vibrational bands of a diatomic molecule excited in an arc flame.

$v$	0	1	2	3	4
$N_v/N_0$	1.000	0.250	0.062	0.016	0.005

Show that the gas is in thermodynamic equilibrium.

Calculate the temperature of the gas, if the vibrational characteristic temperature is 3400 K.

- 8.9 Show that the entropy of an ideal gas in thermal equilibrium is given by the formula

$$S = -k \sum_s [ \langle n_s \rangle \ln n_s \pm \langle 1 \mp n_s \rangle \ln \langle 1 \mp n_s \rangle ]$$

where the upper sign is for FD gas and the lower for BE gas.

- 8.10 Show how the expression (8.90) for the magnetic susceptibility  $\chi$  can be obtained by finding the average magnetic moment of the molecules in the direction of the field applied.

- 8.11 The concentration of electrons in a gas discharge at temperature 2000 K is  $n = 10^{18} \text{ m}^{-3}$ . Find the pressure of electrons.



S.N. Bose, considering thermal radiation as a gas of photons, introduced in 1924 the concept of their indistinguishability and obtained Planck's formula. Subsequently Einstein developed this idea further into what is now known as Bose-Einstein statistics.

### 9.1 PHOTON GAS

Consider an enclosure containing electromagnetic radiation. If the enclosure is maintained at a temperature  $T$ , it will emit and re-absorb photons. After a certain lapse of time, a situation will be established in which the photons and the matter of which the cavity is composed, will be in thermodynamic equilibrium. The number of photons in such an enclosure is not definite; but its total energy remains constant. The electromagnetic radiation within the enclosure is called *black-body radiation*. In this section we will discuss the properties of this radiation.

(i) **Radiation pressure:** Such a radiation may be regarded as a gas of photons. The state of a photon can be specified by the magnitude and direction of its momentum and by the direction of polarization of the electromagnetic wave associated with it. If the wave is regarded as quantized, then the photon is considered as a relativistic particle of energy  $\epsilon = \hbar\omega$  and momentum  $|P| = \frac{\hbar\omega}{c}$ . The photons have integral spin and, hence, the photon gas obeys Bose statistics.

Since the gas is in equilibrium, its free energy must be minimum.

$$\text{Therefore, } \frac{\partial F}{\partial N} = 0$$

Thus, the chemical potential of photon gas  $\mu = 0$ . The grand partition function  $Z$ , therefore, is given by

$$Z = \sum_s e^{-\beta n_s \epsilon_s} = \prod_s [1 - e^{-\beta \epsilon_s}]^{-1} \quad \dots(9.1)$$

or

$$\ln Z = - \sum_s \ln [1 - e^{-\beta \epsilon_s}]$$

$$= - \sum_s \ln [1 - e^{-\beta \hbar \omega_s}] \quad \dots(9.2)$$

The number of allowed states with momentum between  $p$  and  $p + dp$  is,  $\frac{V}{2\pi^2 \hbar^3} p^2 dp$ . Or in terms of angular frequency  $\omega$  the number is

$$\frac{V}{2\pi^2 \hbar^3} \cdot \frac{\hbar^2 \omega^2}{c^2} \cdot \frac{\hbar}{c} d\omega = \frac{V}{2\pi^2 c^3} \omega^2 d\omega \quad \dots(9.3)$$

However, in the photon gas, there are two independent directions of polarization of the electromagnetic wave perpendicular to its direction of propagation. Each photon may have one of these directions of polarization and, hence, the number of allowed states is doubled, i.e. it is equal to

$$\frac{V \omega^2}{\pi^2 c^3} d\omega$$

Therefore, the number of allowed states per unit volume is

$$\frac{\omega^2 d\omega}{\pi^2 c^3} \quad \dots(9.4)$$

Replacing the summation by integration, Eq. (9.2) can be written as

$$\ln Z = - \frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 \ln \{1 - e^{-\beta \hbar \omega}\} d\omega \quad \dots(9.5)$$

Integrating by parts

$$\begin{aligned} \ln Z &= \left[ - \frac{V}{\pi^2 c^3} \cdot \frac{\omega^3}{3} \ln \{1 - e^{-\beta \hbar \omega}\} \right]_0^\infty \\ &\quad + \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{3} \cdot \frac{\beta \hbar e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} d\omega \end{aligned}$$

The first term vanishes at both the limits.

$$\text{Therefore } \ln Z = \frac{V \beta \hbar}{3 \pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta \hbar \omega} - 1} d\omega \quad \dots(9.6)$$

Substituting

$$\beta \hbar \omega = x$$

$$\ln Z = \frac{V}{3 \pi^2 c^3 \beta^3 \hbar^3} \int_0^\infty \frac{x^3}{e^x - 1} dx$$

$$= \frac{V}{3 \pi^2 c^3 \beta^3 \hbar^3} \frac{\pi^4}{15} \text{ (see Appendix B)}$$

$$= \frac{V\pi^2}{45} \left( \frac{kT}{\hbar c} \right)^3 \quad \dots(9.7)$$

Now  $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = kT^2 \frac{\partial \ln Z}{\partial T}$

$$= \frac{V\pi^2}{15} \cdot \frac{(kT)^4}{\hbar^3 c^3} \quad \dots(9.8)$$

and  $\langle P \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{\pi^2}{45} \frac{(kT)^4}{\hbar^3 c^3} \quad \dots(9.9)$

Therefore  $\langle P \rangle V = \frac{1}{3} \langle E \rangle$ , i.e.  $\langle P \rangle = \frac{1}{3} \frac{\langle E \rangle}{V}$

Thus, the pressure of the radiation is equal to one-third of the energy density, a well-known result of the radiation theory.

Note that the corresponding relation for the gas of material particles is

$$pV = \frac{2}{3} E \quad \dots(9.10)$$

Can you account for the difference in the behaviour of these two gases (Prob. 9.1)?

Entropy of the thermal photons is

$$\begin{aligned} S &= k[\ln Z + \beta \langle E \rangle] \\ &= k \left[ \frac{V\pi^2}{45} \left( \frac{kT}{\hbar c} \right)^3 + \frac{V\pi^2}{15} \left( \frac{kT}{\hbar c} \right)^3 \right] \\ &= \frac{4V\pi^2 k^4 T^3}{45 \hbar^3 c^3} \quad \dots(9.11) \end{aligned}$$

Sakur-Tetrode equations [Eq. (6.91)] shows that the entropy is of the order of number of particles. It is believed that in the universe the number of photons is  $10^8$  times larger than the total number of molecules. Photons, therefore, provide dominant contribution to the entropy of the universe, although the particles dominate the total energy.

**(ii) Radiation density:** Since the number of states per unit volume, in the range of frequency  $\omega$  and  $\omega + d\omega$ , is  $\frac{\omega^2 d\omega}{\pi^2 c^3}$  the energy density per frequency interval  $d\omega$  is

$$\begin{aligned} p(\omega, T) d\omega &= \frac{\omega^2 d\omega}{\pi^2 c^3} \langle n_\omega \rangle \hbar \omega \\ &= \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar \omega/kT} - 1} d\omega \quad \dots(9.12) \end{aligned}$$

$$\text{Therefore } \rho(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} \cdot \frac{1}{e^{\hbar\omega/kT} - 1} \quad \dots(9.13)$$

which is Planck's radiation law. The variation of  $\rho(\omega, T)$  as a function of  $\omega$  and also of  $T$  is shown in Fig. 9.1.

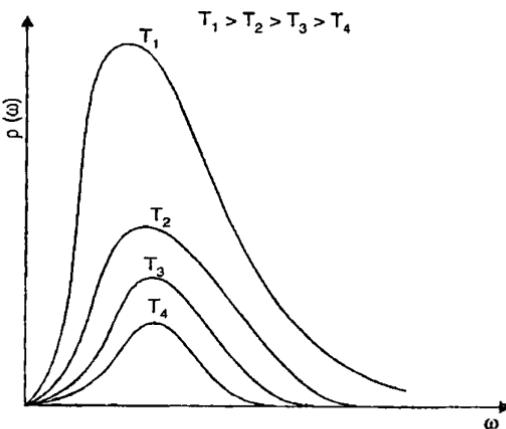


Fig. 9.1

When  $\frac{\hbar\omega}{kT} \ll 1$ , expanding the exponential and neglecting higher powers, Eq. (9.12) reduces to

$$\rho(\omega, T) d\omega = \frac{\omega^2 kT}{\pi^2 c^3} d\omega \quad \dots(9.14)$$

This is *Rayleigh-Jeans law*.

When  $\hbar\omega/kT \gg 1$ , we have

$$\rho(\omega, T) d\omega = \frac{\hbar\omega^3}{\pi^2 C^3} e^{-\hbar\omega/kT} d\omega \quad \dots(9.15)$$

which is Wien's law.

(iii) **Emissivity:** If a small hole is made in the side of the cavity, some of the electromagnetic energy will be radiated. The amount of energy coming out per unit area per unit time is called the *black-body emissivity*.

Let us calculate the radiation emitted through the hole. A section of cavity near the hole is shown in Fig. 9.2. The photons that are emitted through the hole in a short time  $\Delta t$  must be located inside a hemisphere of radius  $R = c\Delta t$  and must be directed towards the hole. Imagine an elementary toroid of section  $rd\theta dr$  at a distance  $r$  from the hole and inside the hemisphere. The volume of the elementary toroid is  $2\pi r \sin \theta rd\theta dr$  and its energy content is  $2\pi r \sin \theta rd\theta dr \rho(\omega)d\omega$ , where  $\rho(\omega)$  is the density of radiation of frequency between  $\omega$  and  $\omega + d\omega$ . Now if  $\Delta S$  is the area of the hole, the angle subtended by  $\Delta S$  as the element of toroid is

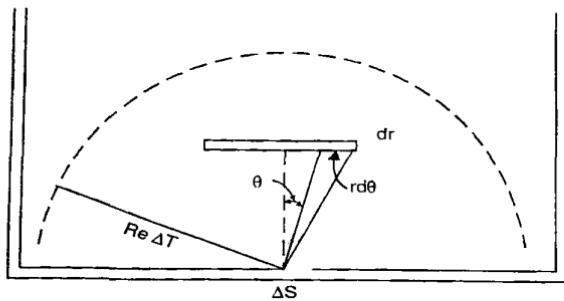


Fig. 9.2

$$d\Omega = \frac{\Delta S \cos \theta}{r^2} \quad \dots(9.16)$$

Since all photon directions are in the solid angle  $\Omega = 4\pi$ , the probability that the photons are directed towards  $\Delta S$  is

$$\frac{d\Omega}{\Omega} = \frac{\Delta S \cos \theta}{4\pi r^2} \quad \dots(9.17)$$

Therefore, the energy that leaks from the toroid through the hole is

$$\begin{aligned} &= 2\pi r \sin \theta dr d\theta d\rho(\omega) d\omega \frac{\Delta S \cos \theta}{r^2} \\ &= \frac{\rho(\omega) \Delta S d\omega}{2} \sin \theta \cos \theta d\theta dr \end{aligned} \quad \dots(9.18)$$

(per unit solid angle).

Hence, the energy from the cavity that leaks through the hole

$$\begin{aligned} &= \int_0^{R=c\Delta t} \int_0^{\pi/2} \frac{\rho(\omega) \Delta S d\omega}{2} \sin \theta \cos \theta d\theta ds \\ &= \frac{\rho(\omega) \Delta S d\omega c \Delta t}{4} \end{aligned} \quad \dots(9.19)$$

The energy, that leaks through unit area per unit time, is  $= \frac{1}{4} \rho(\omega) c d\omega$ .

Hence

$$e(\omega, T) = \frac{1}{4} \rho(\omega) c d\omega = f \frac{1}{4} \frac{\hbar \omega^3}{\pi^2 c^2} \frac{1}{e^{\hbar \omega/kT} - 1} d\omega \quad \dots(9.20)$$

The total energy radiated per unit area per unit time is

$$E_{rad} = \int_0^{\infty} \frac{\hbar \omega^3}{4\pi^2 c^2} \cdot \frac{1}{e^{\hbar \omega/kT} - 1} d\omega$$

$$= \frac{h}{4\pi^2 c^2} \left( \frac{kT}{h} \right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx$$

(where we have put  $x = \hbar\omega/kT$ )

$$\begin{aligned} &= \frac{h}{4\pi^2 c^2} \left( \frac{kT}{h} \right)^4 \frac{\pi^4}{15} \\ &= \frac{k^4 \pi^2}{60 c^2 h^3} T^4 = \sigma T^4 \end{aligned} \quad \dots(9.21)$$

where  $\sigma = \frac{k^4 \pi^2}{60 c^2 h^3} = 5.67 \times 10^{-8} \text{W/m}^2 \text{K}^4$   $\dots(9.22)$

This is known as Stefan's law and  $\sigma$  as Stefan-Boltzmann constant.

**(iv) Equilibrium number of photons in the radiation cavity:** Since the radiation density in the frequency interval  $\omega$  to  $\omega + d\omega$  is  $\rho(\omega, T) d\omega$  the number of photons, each with energy  $\hbar\omega$ , per unit volume is

$$\frac{\rho(\omega, T) d\omega}{\hbar\omega}$$

Therefore

$$\begin{aligned} N &= \int_0^\infty \frac{V}{\hbar\omega} \cdot \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1} d\omega \\ &= \frac{V}{\pi^2 c^3} \left( \frac{kT}{\hbar} \right)^3 \int_0^\infty \frac{x^3}{e^x - 1} dx \left( x = \frac{\hbar\omega}{kT} \right) \\ &= \frac{2.404 V k^3 T^3}{\pi^2 c^3 \hbar^3} \end{aligned} \quad \dots(9.23)$$

Therefore, the equilibrium number of photons in the cavity is given by

$$N \propto VT^3 \quad \dots(9.24)$$

## 9.2 EINSTEIN'S DERIVATION OF PLANCK'S LAW

Einstein gave a simplified statistical method for deriving Planck's formula (9.18) by considering a system of oscillators, and radiators in equilibrium in an isothermal enclosure.

We begin by considering two levels. Figure 9.3 shows two energy levels  $E_1$  and  $E_2$ , populated, respectively, by  $N_1$  and  $N_2$  atoms per unit volume.

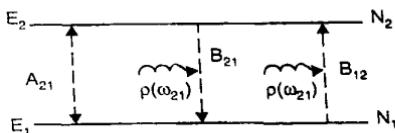


Fig. 9.3

There are three possible radiative processes connecting the two levels:

- (i) In the presence of radiation of density  $\rho(\omega_{21})$  of appropriate frequency, an atom in level 1 may absorb energy  $\hbar\omega_{21}$  and jump to level 2. The number of atoms undergoing this transition will be proportional to the population  $N_1$ , to the external radiation density  $\rho(\omega_{21})$  and to the probability of transition in unit time  $B_{12}$ . The number of such transitions, therefore, is  $B_{12} N_1 \rho \text{ sec}^{-1} \text{ m}^{-3}$ .
- (ii) An atom in level 2 may undergo a spontaneous transition to level 1, with emission of energy  $\hbar\omega_{21}$ , its probability in unit time being  $A_{21}$ . The number of such transitions is  $= N_2 A_{21}$ . Radiations of this type are in random directions and in random phases and, hence, are incoherent.
- (iii) An atom in state 2, in the presence of radiation may undergo an induced transition to level 1 with emission of energy  $\hbar\omega_{21}$ . The probability for this transition is denoted by  $B_{21}$  and the number of atoms undergoing this transition is  $B_{21} N_2 \rho(\omega_{21})$ . The induced radiation will have the same direction and phase as the stimulating radiation and, hence, is coherent.

When thermodynamic equilibrium is reached, the rate at which the atoms enter level 2 must equal the rate at which they leave it.

$$\text{Therefore } N_1 B_{12} \rho(\omega_{21}) = N_2 A_{21} + N_2 B_{21} \rho(\omega_{12}) \quad \dots(9.25)$$

$$\text{or } \rho(\omega_{21}) = \frac{N_2 A_{21}}{N_1 B_{12} - N_2 B_{21}} = \frac{A_{21}}{B_{21} \left( \frac{N_1}{N_2} \frac{B_{12}}{B_{21}} - 1 \right)} \quad \dots(9.26)$$

Assuming that the distribution of atoms in various levels is Boltzmann distribution

$$\frac{N_1}{N_2} = \frac{g_1 e^{-E_1/kT}}{g_2 e^{-E_2/kT}} = \frac{g_1}{g_2} e^{(E_2 - E_1)/kT} = \frac{g_1}{g_2} e^{\hbar\omega_{21}/kT} \quad \dots(9.27)$$

where  $\hbar\omega_{21} = E_2 - E_1$  and  $g_1, g_2$  are the degeneracies of the two levels.

$$\text{Therefore } \rho(\omega_{21}) = \frac{A_{21} B_{21}}{\frac{g_1}{g_2} \frac{B_{12}}{B_{21}} e^{\hbar\omega_{21}/kT} - 1} \quad \dots(9.28)$$

This should be identical with Planck's expression ,

$$\rho(\omega_{21}) = \frac{\hbar\omega_{21}^3}{\pi^2 c^3} \cdot \frac{1}{e^{\hbar\omega_{21}/kT} - 1} \quad \dots(9.29)$$

Equation (9.28) will be identical with Eq. (9.29), only if

$$g_1 B_{12} = g_2 B_{21} \quad \dots(9.30)$$

and  $A_{21} = \frac{\hbar \omega_{21}^3}{\pi^2 c^3} B_{21}$  ... (9.31)

These relations connect the three coefficients  $A_{21}$ ,  $B_{21}$ ,  $B_{12}$  which are called *Einstein's coefficient of spontaneous emission, induced emission and induced absorption, respectively, and are intrinsic atomic properties.*

If an assembly of atoms which have energy levels (1) and (2) as in Fig. 9.3 are irradiated with light of frequency  $\omega_{21}$ , every atom in level (1) has a probability of capturing a photon and thus attenuating the light, whereas every atom in level (2) has a probability of adding a photon and thus amplifying the light. The emerging radiation will have intensity proportional to

$$(N_2 - N_1)\rho\omega_{21}B_{21} \quad \dots(9.32)$$

if spontaneous emissions are eliminated. This intensity will be reduced or amplified with respect to the incident radiation, according as

$$\begin{aligned} N_2 &< N_1 \\ \text{or} \quad N_2 &> N_1 \end{aligned} \quad \dots(9.33)$$

Normally there are more atoms in level (1) than in (2), so that in thermal equilibrium absorption overrides stimulated emission, by a factor

$e^{\hbar\omega/kT}$ . To obtain a net amplification,  $N_2$  must be greater than  $N_1$ . This is non-equilibrium situation and is known as '*population inversion*'. Two devices have been built around this process: (1) The *Maser* (Microwave Amplification by Stimulated Emission of Radiation) and (2) *Laser* (Light Amplification by Stimulated Emission of Radiation). The first works in the microwave region and the second in the optical region. The amplification in some case is so powerful as to produce highly monochromatic flux of several megawatts per square metre.

### 9.3 BOSE-EINSTEIN CONDENSATION

The ideal Bose-Einstein gas is particularly interesting because it can undergo a phase transition.

We have seen that the average number of bosons in the energy state  $\epsilon_s$  is given by

$$\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1}$$

Since  $\Sigma \langle n_s \rangle = N$

$$N = \sum_s \frac{1}{e^{\beta(\epsilon_s - \mu)} - 1} \quad \dots(9.34)$$

or replacing the summation by integration

$$N = \frac{V}{2\pi^2 \hbar^3} \int_0^\infty \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1} p^2 dp \quad \dots(9.35)$$

We have also shown in the preceding chapter that BE distribution goes over to MB distribution when  $e^{-\beta\mu} \gg 1$ , i.e. Eq. (9.36). Therefore

$$\left( \frac{2\pi m k T}{\hbar^2} \right)^{3/2} \left( \frac{V}{N} \right) \gg 1$$

This condition is satisfied when  $T$  is high. Therefore, at high temperatures  $\mu$  is large and negative (see Eq. (6.95)). With the decrease in temperature, the magnitude of  $\mu$  also decreases. At what temperature will  $\mu$  be equal to zero? To answer this question we put  $\mu = 0$  in Eq. (9.35) and denote the corresponding temperature by  $T_b$ .

$$\text{Therefore } N = \frac{V}{2\pi^2 \hbar^3} \int_0^\infty \frac{p^2 dp}{e^{p^2/2mkT_b} - 1} \quad \dots(9.36)$$

$$\text{Let } x^2 = p^2/2mkT_b$$

Substituting in Eq. (9.37)

$$N = \frac{V}{2\pi^2 \hbar^3} (2mkT_b)^{3/2} \int_0^\infty \frac{x^2}{e^{x^2} - 1} dx \quad \dots(9.37)$$

$$= \frac{V}{2\pi^2 \hbar^3} (2mkT_b)^{3/2} \times 2.612 \frac{\pi^{1/2}}{4}$$

(see Appendix B) ... (9.38)

$$\text{Therefore } T_b = \frac{2\pi\hbar^2}{mk} \left( \frac{N}{2.612 V} \right)^{2/3} \quad \dots(9.39)$$

$T_b$ , therefore, is a characteristic temperature that depends on particle mass  $m$  and particle density  $N/V$  and is known as *Bose temperature*.

What will happen if the temperature is further reduced?  $\mu$  cannot be positive nor can it become negative again. The only possibility is for  $\mu$  to remain equal to zero after it has attained zero value.

The variation of  $\mu$  of the ideal boson gas is shown in Fig. 9.4.

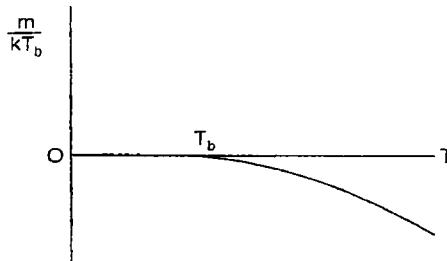


Fig. 9.4

A difficulty creeps in at this stage. The very first term, i.e. the ground state term with  $\epsilon_s = 0$  — in the summation of Eq. (9.34) tends to infinity if  $\mu = 0$ . The reason for this contradiction is the following: For a boson gas, there is no limitation on the number of particles that can belong to a single state, and, yet, the ground state was given zero weight as is evident from the fact that while replacing summation by integration, the density of states which it contained is proportional to  $Vd^3p$ , i.e. to  $V\sqrt{\epsilon} d\epsilon$  and which vanishes at  $\epsilon = 0$ .

To remove this contradiction, we isolate the population of the ground state  $N$  in a separate term and write

$$N = N_0 + \frac{V}{2\pi^2\hbar^3} \int_0^\infty \frac{p^2 dp}{e^{B(p^2 - \mu)} - 1} \quad \dots(9.40)$$

The integral is for excited states  $\epsilon = 0$ . The lower limit can still be taken as zero, since it does not contribute towards the integral.

Integrating as before

$$N = N_0 + \frac{V}{2\pi^2\hbar^3} (2mkT)^{3/2} \times 2.612 \frac{\sqrt{\pi}}{4} \quad \dots(9.41)$$

Substituting for  $V$  from Eq. (9.39)

$$N = N_0 + \frac{(2mkT)^{3/2}}{2\pi^2\hbar^3} \times 2.612 \times \frac{\sqrt{\pi}}{4} \times \left( \frac{2\pi\hbar^2}{mk} \right)^{3/2} \frac{N}{2.612 T_b^{3/2}} \quad \dots(9.42)$$

$$= N_0 + N \left( \frac{T}{T_b} \right)^{3/2}$$

Therefore 
$$N_0 = N \left\{ 1 - \left( \frac{T}{T_b} \right)^{3/2} \right\} \quad \dots(9.43)$$

At  $T \rightarrow 0$ ,  $N_0 \rightarrow N$ , all bosons at  $T = 0$  are in the ground state. This macroscopic occupation of the zero momentum ground state is called *Bose-Einstein condensation* of bosons. It may be noted that we are referring here to the 'condensation' in the momentum space, and not to the actual condensation in the gas. As  $T$  increases, the number of particles in the ground state decreases, the remaining particles being distributed into other states.

For  $T < T_b$  the system may be regarded as a mixture of two phases: (i) a gaseous phase with  $N' = N(T/T_b)^{3/2}$  particles distributed over the excited states, i.e. state for which  $\epsilon \neq 0$  and (ii) a condensed phase with  $N_0 = N - N'$  particles in the ground state, with  $\epsilon = 0$ . For  $T > T_b$  the system will be in the gaseous phase alone.

For  $T < T_b$ , since the particles in the ground state ( $\epsilon = 0$ ) do not contribute to the energy, the total energy is determined by the particles in excited state  $\epsilon > 0$ .

$$\text{Therefore } E = N' \epsilon = \frac{V}{2\pi^2 \hbar^2} \int \frac{p^2}{2m} \frac{p^2 dp}{e^{p^2/2mkT} - 1}$$

$$= \frac{V}{2\pi^2 \hbar^3} \frac{(2mkT)^{5/2}}{2m} \int_0^\infty \frac{x^4}{e^{x^2} - 1} dx$$

$$= \frac{V}{2\pi^2 \hbar^3} (2m)^{3/2} k^{5/2} T^{5/2} \times \frac{3}{8} \times 1.341 \sqrt{\pi}$$

(see Appendix B)

$$= \frac{3}{16} \frac{1.341 V (2m)^{3/2} k^{5/2} T^{5/2}}{\pi^{3/2} \hbar^3} \quad \dots(9.44)$$

Substituting for  $V$  from Eq. (9.39)

$$E = 0.77 N k \frac{T^{5/2}}{T_b^{3/2}} \quad \dots(9.45)$$

The heat capacity of the ideal boson gas can be determined from the equation

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 1.93 N k \frac{T^{3/2}}{T_b^{3/2}} \quad \dots(9.46)$$

We see from Eq. (9.46) that at the condensation temperature  $T = T_b$  the heat capacity exceeds the classical value  $\frac{3}{2} Nk$ . The variation of  $C_V$  with  $T$  is shown in Fig. 9.5.

Now  $pV = \frac{2}{3} E$ . Substituting for  $E$  from Eq. (9.44).

$$p_{(T)} = \frac{1.341 (2m)^{3/2} k^{3/2} T^{5/2}}{8\pi^{3/2} \hbar^3} \quad \dots(9.47)$$

Substituting for  $m$  from Eq. (9.39)

$$p_{(T)} = \frac{1.341 k T^{5/2}}{2.612 T_b^{3/2}} \left( \frac{N}{V} \right) \quad \dots(9.48)$$

Therefore pressure at the transition point, i.e. at  $T = T_b$

$$p_{(T_b)} = 0.5134 \left( \frac{N}{V} k T_b \right) \quad \dots(9.49)$$

Thus the pressure of an ideal Bose gas at the transition temperature  $T_b$  is about one-half of that of an equivalent Boltzmann gas. From Eqs.

(9.48) and (9.49), we find that for  $T \leq T_b$

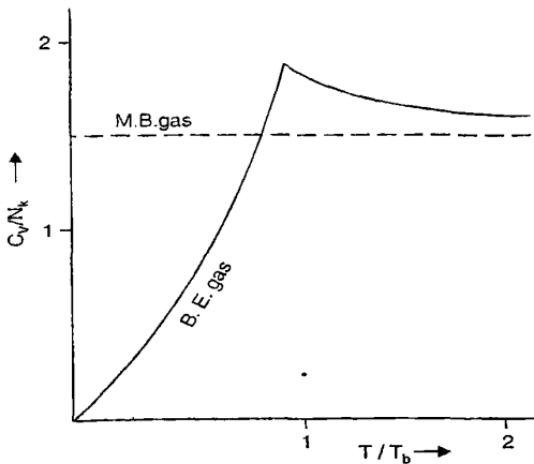


Fig. 9.5

$$\frac{P(T)}{P(T_b)} = \left( \frac{T}{T_b} \right)^{5/2} \quad \dots(9.50)$$

Therefore  $P(T) = P(T_b) \left( \frac{T}{T_b} \right)^{5/2} = 0.5134 \left( \frac{NkT_b}{V} \right) \left( \frac{T}{T_b} \right)^{5/2}$

$$\begin{aligned} &= 0.5134 \left\{ N \left( \frac{T}{T_b} \right)^{3/2} \right\} \frac{kT}{V} \\ &= 0.5134 \frac{N' k T}{V} \end{aligned} \quad \dots(9.51)$$

We conclude, therefore, that the particles in the condensed phase do not exert any pressure, but the pressure exerted by the particles in the excited state is about half of the pressure that would have been exerted if the gas were Boltzmannian.

Entropy of the boson gas is most expeditiously obtained from the relation

$$E = TS - pV + \mu N \quad \dots(9.52)$$

Since  $\mu = 0$

$$S = \frac{E + pV}{T} = \frac{5}{2} \frac{pV}{T} \left( \text{because, } pV = \frac{2}{3} E \right)$$

$$= \frac{5}{2} \times 0.5134 N' k \left( \frac{T}{T_b} \right)^{3/2} \quad \dots(9.53)$$

where we have used Eq. (9.51).

It is known that a peculiar phase transition occurs in liquid helium at 2.19 K.  ${}^4\text{He}$  obeys Bose statistics. However, the Bose distribution, which relates to ideal gases, cannot be applied to liquid helium. Nevertheless, it would be interesting to compare the actual temperature of transition in liquid helium with the temperature at which Bose condensation would occur in gaseous helium of the same density.

For liquid  ${}^4\text{He}$ ,  $m = 6.65 \times 10^{-22} \text{ kg}$   
and  $V = 22.4 \times 10^{-23} \text{ m}^3/\text{mole}$

Substituting these in Eq. (9.39)

$$T_b = 3.14 \text{ K}$$

which is close to transition temperature.

## 9.4 SPECIFIC HEAT FROM LATTICE VIBRATION

We have seen that the dilute gases can be regarded as ideal gases and their thermodynamic properties can be successfully discussed by the methods of statistical mechanics. Liquids and dense gases are difficult to handle because of the intermolecular forces which play an important role. In a crystalline solid, the atoms are very close; but such a system is well-ordered. We will show in this section how the properties of the simplest of these systems, the monatomic solids, can be discussed using the techniques of statistical mechanics.

A monatomic solid consists of a large number of atoms in regular array, a lattice. Because of thermal agitation each atom vibrates about its equilibrium position.

The specific heat of a substance is one of the most important thermodynamic quantities. Various factors contribute to the specific heat. However, the dominant contribution in most solids is the energy given to the lattice vibrations.

Consider a solid containing  $N$  non-interacting particles harmonically bound to centres of forces. The Hamiltonian of each atom is

$$H = \sum_{i=1}^3 \frac{p_i^2}{2m} + \sum_{i=1}^3 \frac{1}{2} k q_i^2 \quad \dots(9.54)$$

By the theorem of equipartition of energy

$$\text{Energy/atom} = 6 \times \frac{1}{2} kT = 3kT$$

and the total energy for  $N$  atoms  $E = 3 N kT$ , where  $N$  is Avogadro's number

$$\begin{aligned} \text{Therefore } C_v &= 3 Nk = 3 R \equiv 5.96 \text{ cal/mole.} \\ &\equiv 24.93 \text{ J/mole.} \end{aligned} \quad \dots(9.55)$$

This result asserts that all simple solids have the same molar specific heat equal to  $5.96 \text{ cal mole}^{-1} \text{ deg}^{-1} = 24.93 \text{ J mole}^{-1} \text{ deg}^{-1}$ . This is known as the law of Dulong and Petit.

It was noticed, however, that the specific heat of most materials decreases as the temperature is lowered. Diamond, for example, has as low a value of  $C_p$  as 1.1 even at 300 K. Classical statistical mechanics could not explain this variation of the specific heat with temperature.

Einstein was the first to apply quantum concept to the theory of specific heat of solids. He made the most simplifying assumption that all  $3N$  vibrational modes of a three-dimensional solid of  $N$  atoms have the same frequency. The energy levels of the oscillator are quantized.

$$\text{Therefore } \varepsilon_n = \left( n + \frac{1}{2} \right) \hbar\omega \quad \dots(9.56)$$

The partition function  $Z$  is

$$Z = \sum_{n=0}^{\infty} e^{-\beta \left( n + \frac{1}{2} \right) \hbar\omega} = e^{-\beta \frac{\hbar\omega}{2}} \frac{1}{1 - e^{-\beta \hbar\omega}} \quad \dots(9.57)$$

or

$$\begin{aligned} \ln Z &= -\frac{\beta}{2} \hbar\omega - \ln(1 - e^{-\beta \hbar\omega}) \\ \langle \varepsilon \rangle &= -\frac{\beta}{2} \hbar\omega - \ln(1 - e^{-\beta \hbar\omega}) \\ &= -\frac{1}{2} \hbar\omega + \frac{e^{-\hbar\omega/kT} \hbar\omega}{1 - e^{-\hbar\omega/kT}} \end{aligned} \quad \dots(9.58)$$

Thus, the total mean energy is

$$\langle E \rangle = 3N\hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1} \right) \quad \dots(9.59)$$

and

$$\begin{aligned} C_v &= \left( \frac{\partial \langle E \rangle}{\partial T} \right)_V = \frac{3N\hbar\omega e^{\hbar\omega/kT} (\hbar\omega/kT)^2}{(e^{\hbar\omega/kT} - 1)^2} \\ &= \frac{3N\hbar^2\omega^2 e^{\hbar\omega/kT}}{kT^2 (e^{\hbar\omega/kT} - 1)^2} = 3Nk \left( \frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \end{aligned} \quad \dots(9.60)$$

where  $\theta_E = \frac{\hbar\omega}{k}$  is called Einstein characteristic temperature.

Now if  $T \gg \theta_E$ , i.e.  $\frac{\theta_E}{T} \ll 1$

we can write  $e^{\theta_E/T} = 1 + \frac{\theta_E}{T} + \frac{1}{2}\left(\frac{\theta_E}{T}\right)^2 + \dots$

Therefore, from Eq. (9.60)

$$\begin{aligned} C_v &= 3Nk\left(\frac{\theta_E}{T}\right)^2 \cdot \frac{1 + \theta_E/T}{\left(\theta_E/T\right)^2} \\ &= 3Nk + 3Nk(\theta_E/T) \approx 3R \end{aligned} \quad \dots(9.61)$$

Thus, at high temperature, the result tends towards the classical one. On the other hand, if  $T \ll \theta_E$ , i.e.  $\frac{\theta_E}{T} \gg 1$

$$C_v = 3Nk\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \quad \dots(9.62)$$

The specific heat, therefore, falls at an exponentially fast rate and tends to zero at  $T \rightarrow 0$ . Einstein's theory, thus explained for the first time why the molar specific heat decreases with temperature. This variation is shown in Fig. 9.6. The specific heat tends to zero at absolute zero and rises to the classical value at high temperatures. The shaded area is equal to the zero-point energy. Can you prove this (Prob. 9.6)?

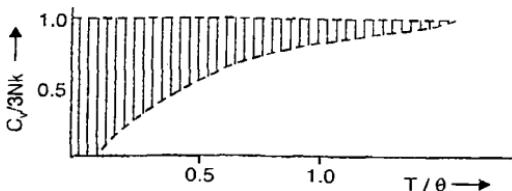


Fig. 9.6

The rate of fall, however, turns out to be too fast in comparison with the observed rate. In fact, it has been observed experimentally that  $C_v \propto T^3$  as  $T \rightarrow 0$ . We have to account for this discrepancy.

## 9.5 DEBYE'S MODEL OF SOLIDS : PHONON GAS

The discrepancy referred to in the preceding section is due to the assumption that all atoms vibrate with the same frequency. In reality, if a solid has  $N$  atoms, it has  $3N$  normal modes of vibration and, hence  $3N$  different frequencies. To remove the deficiencies of the Einstein model, we need a more realistic appraisal of the actual distribution of frequencies.

In the improved model suggested by Debye, the discreteness of the atoms in the solid is neglected and the solid is treated as if it were a continuous elastic medium, each normal mode of vibration of the elastic continuum being characterised by a frequency  $\omega$ . If the temperature is not too high, amplitudes of vibration of individual atoms in a solid are

relatively small and collective modes of vibration involving groups of atoms are the possible sound waves which can propagate through solids. The energy of these sound waves inside a solid medium can be considered to be quantized in the form of phonons just as the energy of electromagnetic radiation is quantized in the form of *photons*. The energy of a phonon of frequency  $\omega$  is  $\hbar\omega$ . Since the phonons have integral angular momentum and there is no restriction on the number of phonons in a given mode, the assembly of phonons in a solid may be treated as a boson gas with zero chemical potential. However, since we cannot have free phonons in empty space without crystal lattice, phonon is not considered as a true particle. It is sometimes called a *quasiparticle*.

A plane-wave expansion is always possible for the description of the acoustic waves in solids. Three types of plane waves can propagate in a solid; two of these waves have polarization transverse to the direction of propagation  $k$ , and the third has longitudinal polarization along  $k$ . The velocities of propagation in the longitudinal and transverse directions are different. Let us denote them by  $v_L$  and  $v_T$  respectively.

The number of normal modes with frequency between  $\omega$  and  $\omega + d\omega$  is given analogously by

$$\sigma^1(\omega)d\omega = \frac{V\omega^2d\omega}{2\pi^2v_s^3} \quad \dots(9.63)$$

where  $v_s$  is the velocity of the concerned wave. Since there are two transverse and one longitudinal type of vibrations and the transverse mode is doubly degenerate, the total number of modes of vibration in the frequency interval  $\omega$  to  $\omega + d\omega$  will be

$$\sigma(\omega)d\omega = \frac{V\omega^2}{2\pi^2} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right) d\omega \quad \dots(9.64)$$

Debye assumed that the spectrum of frequencies is cut off at an upper limit  $\omega_D$ , such that the total number of normal modes is equal to  $3N$ , i.e.

$$\int_0^{\omega_D} \sigma(\omega)d\omega = 3N \quad \dots(9.65)$$

where  $\omega_D$  is the maximum frequency of phonons in a crystal.

Therefore

$$\int_0^{\omega_D} \frac{V\omega^2}{2\pi^2} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right) d\omega = 3N \quad \dots(9.66)$$

i.e.

$$\frac{V\omega_D^3}{6\pi^2} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right) = 3N$$

and hence

$$\omega_D^3 = \frac{18N\pi^2}{V} \left( \frac{1}{v_L^3} + \frac{2}{v_T^3} \right)^{-1} \quad \dots(9.67)$$

Using Eqs. (9.64) and (9.67), we find that the Debye spectrum is given by

$$\sigma(\omega) = \begin{cases} \frac{9N\omega^2}{\omega_D^3} & \text{for } \omega < \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} \quad \dots(9.68)$$

In Fig. 9.7 we compare the density of states for copper deduced from neutron scattering experiments with those derived from Debye's assumption (dotted curve).

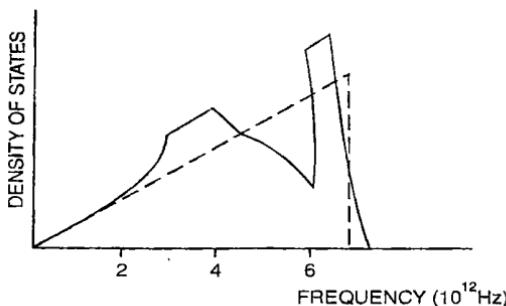


Fig. 9.7

We see that Debye assumption is reasonably valid for low frequency modes. There are serious discrepancies in the region of higher frequencies (optical modes). The actual maximum frequency seems to be quite close to the debye value, but the centre of gravity of the frequency distribution is lowered. These finer details of the spectrum, however, are not very important when we consider averaged quantities such as the specific heat.

Since the number of phonons is not conserved, the chemical potential for phonons,  $\mu = 0$ . Therefore, the distribution law for phonons will be

$$\langle n_s \rangle = \frac{1}{e^{\hbar\omega/kT} - 1} \quad \dots(9.69)$$

The internal energy of the phonon gas

$$\begin{aligned} E &= \int_0^{\omega_D} \hbar\omega \langle n_s \rangle \sigma(\omega) d\omega \\ &= \int_0^{\omega_D} \hbar\omega \cdot \frac{1}{e^{\hbar\omega/kT} - 1} \cdot \frac{9N}{\omega_D^3} \omega^2 d\omega \\ &= \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega \end{aligned} \quad \dots(9.70)$$

Put

$$x = \hbar\omega/kT$$

$$E = \frac{9N\hbar}{\omega_D^3} \left( \frac{kT}{\hbar} \right)^{4\hbar} \int_0^{\theta_D/kT} \frac{x^3}{e^x - 1} dx \quad \dots(9.71)$$

Let

$$\theta_D = \frac{\hbar\omega_D}{k}$$

$\theta_D$  is called *Debye characteristic temperature*.

$$\text{Therefore } E = \frac{9NkT^4}{\theta_D^3} \int_0^{\theta_D/kT} \frac{x^3}{e^x - 1} dx \quad \dots(9.72)$$

Now if  $T \gg \theta_D$ ,  $x_{\max} = \frac{\hbar\omega_D}{kT} = \frac{\theta_D}{T}$  is small and, therefore, expanding the exponential and neglecting the higher powers, we can write

$$\frac{x^3}{e^x - 1} = x^2 \quad \dots(9.73)$$

$$\text{Therefore } E = \frac{9NkT^4}{\theta_D^3} \left[ \frac{x^3}{3} \right]_0^{\theta_D/kT} = \frac{9NkT^4}{\theta_D^3} \frac{\theta_D^3}{3T^3} = 3NkT \quad \dots(9.74)$$

This leads to the Dulong-Petit law

$$C_v = \left( \frac{\partial E}{\partial T} \right)_V = 3Nk = 3R \quad \dots(9.75)$$

Thus, for temperatures greater than the Debye temperature, the lattice behaves classically.

If, on the other hand,  $T \ll \theta_D$ ,  $x \rightarrow \infty$  then

$$\int_0^{\theta_D/kT} \frac{x^3}{e^x - 1} dx = \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15} \quad \dots(9.76)$$

$$\text{Hence } E = \frac{9NkT^4}{\theta_D^3} \frac{\pi^4}{15} = \frac{3}{5} \frac{\pi^4 Nk}{\theta_D^3} T^4 \quad \dots(9.77)$$

and the specific heat

$$C_v = \frac{12}{5} \pi^4 Nk \left( \frac{T}{\theta_D} \right)^3 \quad \dots(9.78)$$

$$\text{Therefore } C_v \propto T^3 \quad \dots(9.79)$$

The general behaviour for the specific heat calculated from the general expression (9.72) for  $E$  is shown in Fig. 9.8.

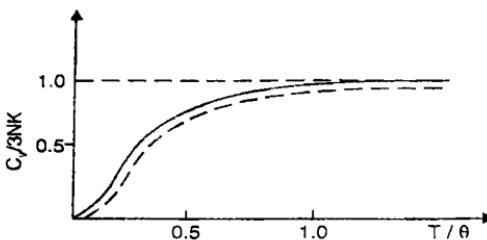


Fig. 9.8

Dotted curve corresponds to the Einstein model.

The specific heat as defined by Eq. (9.78) shows a very good agreement with experimental results.

Some values of  $\theta_D$  are given in Table 9.1.

Table 9.1

Substance	$\theta_D$
Al	426
Cu	335
Na	158
NaCl	321
KCl	235
Diamond	2200

We find from Eq. (9.78) that, although  $\theta_D$  may vary widely from solid to solid, the plot of  $C_v$  against  $T/\theta_D$  should be the same for all monatomic solids.

It must be mentioned here that the Debye model fails at extremely high temperatures, because the forces between atoms are no longer harmonic and the phonons interact strongly with each other.

A question that arises here is that, since sound waves can also exist in liquids, will the quantum effects, discussed above for solids, be manifest in liquids at low temperatures? Two points of importance to be noted in this respect are: (i) liquids can have only longitudinal modes of vibration; they cannot sustain transverse modes as they cannot withstand sheer stress; and (ii) normal modes in liquids may not be purely harmonic. There may also be other excitations in addition to those by phonons, such as vortex flow, turbulence or roton excitation.

Experimentation with liquids is difficult because most liquids freeze long before the temperature is low enough to exhibit the  $T^3$  behaviour. The only exception is liquid helium,  ${}^4\text{He}$ , which remains liquid at very low temperatures. Since liquids can have only longitudinal modes of vibration, the formula (9.78) for  $C_v$  and Eq. (9.67) for  $\omega_D$  reduces to

$$C_v = \frac{4\pi^4}{5} Nk \left( \frac{kT}{\hbar\omega_D} \right)^3 \quad \dots(9.80)$$

and  $\omega_D = \left( \frac{6\pi^2 N}{V} \right)^{1/3} v \quad \dots(9.81)$

where  $v$  is the velocity of sound in the liquid.

Therefore  $C_v = \frac{2\pi^2 k^4 V}{15\hbar^3 v^3} T^3 \quad \dots(9.82)$

Hence, specific heat per gram of the liquid is

$$C_v = \frac{2\pi^2 k^4}{15\rho h^3 v^3} T^3 \quad \dots(9.83)$$

where  $\rho$  is the density of the liquid.

Substituting the value of the density of liquid helium  $\rho = 145.5 \text{ kg/m}^3$  and the velocity of sound  $v = 238 \text{ m/sec}$ , we get

$$C_v = 20.7 T^3 \text{ J/kg/K} \quad \dots(9.84)$$

which agrees fairly well with the experimental value

$$= (20.4 \pm 0.4) T^3 \text{ J/kg/K} \quad \dots(9.85)$$

observed for temperatures  $0 < T < 0.6 \text{ K}$ .

## PROBLEMS

**9.1** The mean pressure of an ideal gas of material particles is related

to its total energy  $E$  by the relation  $\langle p \rangle V = \frac{2}{3} \langle E \rangle$  irrespective of whether the particles obey (BE or FD) statistics; while for photons the relation is  $\langle p \rangle V = \frac{1}{3} \langle E \rangle$ . How do you account for this difference?

**9.2** Find the mean energy per photon in a black-body radiation cavity.

**9.3** Find the mean square fluctuation in the number of photons in an enclosure of a given volume and temperature.

**9.4** A spherical black-body at the initial temperature 1000 K is cooled by radiation. Find the time it will take for the temperature to drop to 100 K.

(Radius of the black-body = 0.1 m

$$\rho = 8 \times 10^3 \text{ kg/m}^3 \text{ and } C_v = 5 \times 10^2 \text{ J/kg/degree}$$

**9.5** Assuming the sun to be a black-body at a temperature 5800 K, calculate

(i) the power received per unit area of the surface of the earth

- (ii) the equilibrium temperature of the earth, assuming it to be an ideal absorber and radiator (Radius of the sun =  $7 \times 10^8$  m)

Distance of the sun from the earth =  $15 \times 10^{10}$  m)

- 9.6** An atom has two electronic states. Set up a equation for the ratio  $N_2/N_1$ , if the atoms obey Bose-Einstein statistics.  $N_1$ ,  $N_2$  are the numbers of atoms in the ground and excited states. Discuss what happens when Bose condensation sets in.
- 9.7** Determine the Bose temperature of bosons each of mass  $6.65 \times 10^{-27}$  kg and spin zero, their concentration being  $10^{26}$  m<sup>-3</sup>.
- 9.8** In the preceding example, determine the fraction  $N_0/N$  of the bosons in the single particle ground state at a temperature  $0.2 T_b$ .



## 10.1 FERMI ENERGY

The Fermi-Dirac distribution function which gives the average occupation of the energy level  $\epsilon$  is given by

$$f(\epsilon) = \langle n_\epsilon \rangle = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} + 1} \quad \dots(10.1)$$

Let us suppose that at  $T = 0$ , the value of  $\mu$  is  $\mu_F$ . When  $T = 0$ ,  $\langle n_\epsilon \rangle$  has two possible values:

$$\begin{aligned} \langle n_\epsilon \rangle &= \frac{1}{e^{-\infty} + 1} = 1 \text{ if } \epsilon < \mu_F \text{ and} \\ &= \frac{1}{e^{\infty} + 1} = 0 \text{ if } \epsilon > \mu_F \end{aligned} \quad \dots(10.2)$$

At absolute zero of temperature, the fermions will necessarily occupy the lowest available energy states. An immediate consequence of the Pauli exclusion principle is that, each quantum state can contain only one fermion. Therefore, all the lowest states will be occupied with one fermion in each, until all the fermions are accommodated. Under this condition the gas is said to be *degenerate*.

$$\langle n_\epsilon \rangle = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} + 1} = \frac{1}{2} - \frac{(\epsilon - \mu)}{4kT} + \dots \quad \dots(10.3)$$

Therefore

$$(i) \text{ If } \epsilon \leq \mu - 2kT \langle n_\epsilon \rangle = 1 \quad \dots(10.4)$$

$$(ii) \text{ If } \epsilon \geq \mu + 2kT \langle n_\epsilon \rangle = 0 \quad \dots(10.5)$$

$$(iii) \text{ If } \epsilon = \mu \langle n_\epsilon \rangle = \frac{1}{2} \quad \dots(10.6)$$

We can show this distribution with varying energy at 0K graphically (Fig. 10.1).

The spread region of Fermi distribution, i.e., the region of  $\epsilon$  when  $\langle n_\epsilon \rangle$  changes from unity to zero (from  $\mu - 2kT$  to  $\mu + 2kT$ ), narrows as the temperature decreases and at absolute zero becomes a sharp discontinuity. The distribution, then, takes the form of a right angle. We see from Fig. 10.1 that, at  $T = 0$ , all states with  $\epsilon < \mu_F$  are occupied;

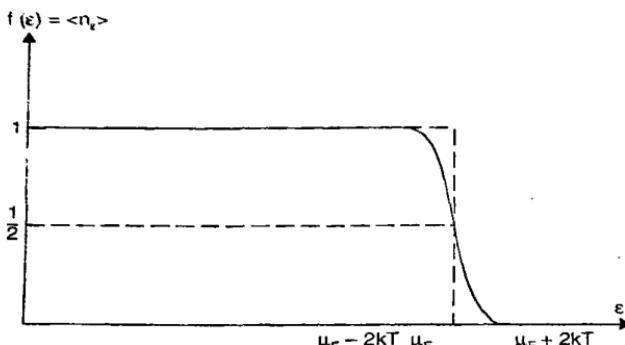


Fig. 10.1

while those with energy  $\epsilon > \mu_F$  are empty. The highest occupied level is called the Fermi level and is represented by  $\epsilon_F$ . Below this level there are exactly  $N$  states, if  $N$  is the total number of fermions. The states above this energy level are unoccupied. The value of  $\epsilon_F$  depends upon the number of fermions in the gas. One can easily see that, at  $T = 0$ ,  $\epsilon_F$  coincides with  $\mu_F$ .

The value of  $\mu_F$  can be found as follows:

$$\int_0^{\infty} n(\epsilon) d\epsilon = N \quad \dots(10.7)$$

where  $N$  is the total number of particles in the gas.

Since at  $T = 0$  all single-particle states up to  $\epsilon_F$  are completely filled with one particle per state,

for  $\epsilon < \epsilon_F$  the number of states  $\sigma(\epsilon) = n(\epsilon)$ ,  
and for  $\epsilon < \epsilon_F$  the number of states  $\sigma(\epsilon) = 0$   $\dots(10.8)$

$$\text{Therefore, } \int_0^{\epsilon_F} \sigma(\epsilon) d\epsilon = N \quad \dots(10.9)$$

If the particles have spin  $s$ , there are  $2s + 1$  single-particle states, all having the same energy  $\epsilon$ . Therefore, the density of states  $\sigma(\epsilon) d\epsilon$  in the energy range from  $\epsilon$  to  $\epsilon + d\epsilon$  is given by

$$\sigma(\epsilon) d\epsilon = \frac{V(2m)^{3/2}(2S+1)}{4\pi^2\hbar^3} d\epsilon \quad \dots(10.10)$$

Hence, Eq. (10.9) can be written as

$$\int_0^{\epsilon_F} \frac{V(2S+1)(2m)^{3/2}}{4\pi\hbar^3} \frac{1}{\epsilon^2} d\epsilon = N \quad \dots(10.11)$$

$$\text{i.e. } \frac{(2S+1)V}{4\pi\hbar^3} (2m)^{3/2} \frac{2}{3} \epsilon_F^{3/2} = N \quad \dots(10.12)$$

$$\text{or } \epsilon_F = \frac{\hbar^2}{2m} \left( \frac{6N\pi^2}{(2S+1)V} \right)^{2/3} \quad \dots(10.13)$$

The value of the single-particle momentum corresponding to the *Fermi energy* is referred to as *Fermi momentum* and is denoted by  $p_F$

$$p_F = \sqrt{2m\epsilon_F} = \hbar \left( \frac{6N\pi^2}{(2S+1)V} \right)^{2/3} \quad \dots(10.14)$$

## 10.2 AN ALTERNATE DERIVATION OF FERMI ENERGY

We give in this section a simpler method of deriving Fermi energy of electron gas. The method is based of Heisenberg's uncertainty principle given by

$$\Delta x \Delta p_x \approx \hbar \quad \dots(10.15)$$

Equation (10.15) can be generalised to all three components as:

$$(\Delta x \Delta p_x) (\Delta y \Delta p_y) (\Delta z \Delta p_z) \approx \hbar^3 \quad \dots(10.16)$$

$$\text{or } (\Delta p_x \Delta p_y \Delta p_z) \approx \frac{\hbar^3}{\Delta x \Delta y \Delta z} \quad \dots(10.17)$$

Considering the momentum volume element  $(\Delta p_x \Delta p_y \Delta p_z)$  as a sphere of radius  $\Delta p$

$$(\Delta p_x \Delta p_y \Delta p_z) = \frac{4}{3} \pi (\Delta p)^3 \approx \frac{\hbar^3}{\Delta V} \quad \dots(10.18)$$

By virtue of the uncertainty principle, each electron occupies at least a volume  $\Delta V$  and this electron can exist in either of the two possible spin orientations.

Therefore, if  $N$  is the number of electrons in a unit volume,  $\Delta V = \frac{2}{N}$

$$\text{Therefore } \frac{4}{3} \pi (\Delta p)^3 \approx \frac{\hbar^3 N}{2} \quad \dots(10.19)$$

\* A. Sankaranarayanan and S. George, *Am. J. Phys.* **40**, 620, 1972.

Hence

$$\Delta p \approx h \left( \frac{3N}{8\pi} \right)^{1/3} \quad \dots(10.20)$$

Since  $\Delta V$  is the minimum volume needed to house an electron,  $\Delta p$  is maximum as a consequence of the uncertainty principle.

Therefore  $\epsilon_F = \frac{(\Delta p)^2}{2m}$  ... (10.21)

$$= \frac{\hbar^2}{2m} \left( \frac{3N}{8\pi} \right)^{2/3} \quad \dots(10.22)$$

which agrees with Eq. (10.13), if  $V = 1$ .

**Example 10.1** The molar mass of lithium is 0.00694 and its density  $0.53 \times 10^3 \text{ kg/m}^3$ . Calculate the Fermi energy and Fermi temperature of the electrons.

Unit volume contains

$$\frac{0.53 \times 10^6}{6.94 \times 10^{-3}} \times 6.02 \times 10^{23} \text{ atoms and as many conduction electrons.}$$

Therefore,  $\frac{N}{V} = 0.4597 \times 10^{32}$

$$\begin{aligned} \epsilon_F &= \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3} \\ &= \frac{1.05^2 \times 10^{-68}}{2 \times 9.1 \times 10^{-31}} \left( 3\pi^2 \times 0.4597 \times 10^{32} \right)^{2/3} \\ &= 7.4 \times 10^{-17} \end{aligned}$$

Hence  $T_F = \frac{\epsilon_F}{k} = 53262 \text{ K}$

We see, therefore, that Fermi temperatures are much higher than the ordinary temperatures. Metals will have melted long before the energy  $kT$  has approached the value of the Fermi energy. This indicates that the electron gas is to be treated as a separate case.

### 10.3 MEAN ENERGY OF FERMIONS AT $T = 0 \text{ K}$

$$\langle \epsilon(0) \rangle = \frac{\int_0^\infty \epsilon n(\epsilon) d\epsilon}{\int_0^\infty n(\epsilon) d\epsilon} \quad \dots(10.23)$$

$$\begin{aligned}
 &= \frac{\int_0^{\epsilon_F} \epsilon \sigma(\epsilon) d\epsilon}{\int_0^{\epsilon_F} \sigma(\epsilon) d\epsilon} \\
 &= \frac{\frac{V(2S+1)(2m)^{3/2}}{4\pi^2 \hbar^3} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon}{\frac{V(2S+1)(2m)^{3/2}}{4\pi^2 \hbar^3} \int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon} \\
 &= \frac{\int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon}{\int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon} = \frac{3}{5} \epsilon_F \quad \dots(10.24)
 \end{aligned}$$

The ground state, or zero-point energy, therefore is

$$E_0 = \frac{3}{5} N \epsilon_F \quad \dots(10.25)$$

Substituting for  $N$  from Eq. (10.13)

$$E_0 = \frac{(2s+1)}{10\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \epsilon_F^{5/2} \quad \dots(10.26)$$

The ground state pressure of the system is

$$p_0 = \frac{2}{3} \left( \frac{E_0}{V} \right) = \frac{2}{5} \frac{N}{V} \epsilon_F = \frac{2}{5} n \epsilon_F \quad \dots(10.27)$$

where

$$n = N/V$$

## 10.4 FERMI GAS IN METALS

Modern theory of electrical conduction in metals began with Paul Drude's paper published in 1900. Drude's theory rests on the assumption that conduction electrons in metals can be treated as a 'gas' of weakly interacting particles. The assumption seems to be absolutely oversimplified. However, it is precisely this feature of Drude's model that forms the basis of the modern theory as well. By applying the methods used in the kinetic theory of gases, Drude was able to give a quantitative derivation of the Wiedemann-Franz law, that the ratio of thermal to electrical conductivities is a universal number (Lorenz number) times the absolute temperature. The calculated Lorenz number was in reasonable agreement with experiment. However, the results for the individual conductivities were not very encouraging. The theory was refined by H.A. Lorenz, who applied MB statistics to the electron gas. He found the theoretical

Lorenz number to be reduced by a factor 2/3 from Drude's value, thus weakening the agreement with experiment. The main drawbacks of Drude's theory are:

- (i) The observed specific heat of metals— $3R$ —at room temperature, appears to be completely accountable by the lattice vibrations alone; while the theory demands that on the basis of the equipartition theorem, every electron must make a contribution of magnitude  $\frac{3}{2}k$  to the specific heat, so that the total capacity should be  $\frac{9}{2}R$ .
- (ii) Failure to explain magnetic properties.
- (iii) Failure to explain the temperature dependence of the conductivity.

The first difficulty was resolved by Sommerfeld by the application of FD statistics to the electron gas in metals. Pauli and Heisenberg showed how quantum theory can be used to explain the negative properties; and the concepts necessary to solve the third problem were provided by Sommerfeld.

Since for electron  $s = \frac{1}{2}$ , Fermi energy and Fermi momentum are given by

$$\epsilon_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3} \quad \dots(10.28)$$

$$p_F = \hbar \left( \frac{3\pi^2 n}{V} \right)^{1/3} \quad \dots(10.29)$$

We define Fermi temperature  $T_F$  by the relation

$$kT_F = \epsilon_F \quad \dots(10.30)$$

## 10.5 ATOMIC NUCLEUS AS AN IDEAL FERMION GAS

Both protons and neutrons are fermions of spin 1/2. Inside the nucleus there are very strong attractive forces between the nucleons. The binding energy of a nucleon in a nucleus is of the order of 8 MeV. Strictly speaking, due to these strong interactions, the protons and neutrons in a nucleus cannot be considered as two non-interacting ideal fermion gases. However, we can get a rough estimate of magnitude for neutrons and protons inside the nucleus, if we assume that they are ideal fermion gases.

An atomic nucleus of atomic weight  $A$  and atomic number  $Z$ , contains  $N = A - Z$  neutrons. The concentration of neutrons in the nucleus is given by

$$\frac{N}{V} = \frac{A-Z}{V} = \frac{A-Z}{\frac{4}{3}\pi R^3} \quad \dots(10.31)$$

where  $R$  is the radius of the nucleus. Experiments in scattering of high energy particles have shown that

$$R = 1.3 \times 10^{-15} \times A^{1/3} \text{ metre} \quad \dots(10.32)$$

$$\begin{aligned} \text{Therefore } \frac{N}{V} &= \frac{3}{4\pi \times (1.3)^3 \times 10^{-45}} \frac{A-Z}{A} \\ &= 1.087 \times 10^{44} \left( \frac{A-Z}{A} \right) \end{aligned} \quad \dots(10.33)$$

For a light nucleus, we can take

$$\frac{A-Z}{A} = 0.5$$

$$\begin{aligned} \text{Therefore } \epsilon_F &= \frac{\hbar^2}{2m} \left( \frac{6\pi^2}{2} \cdot \frac{N}{v} \right)^{2/3} \\ &= \frac{(1.05)^2 \times 10^{-68}}{2 \times 1.67 \times 10^{-27}} \left( \frac{6\pi^2}{2} \times 1.087 \times 10^{44} \times 0.5 \right)^{2/3} \end{aligned}$$

(Here, mass of neutron =  $1.67 \times 10^{-27}$  kg)

$$\epsilon_F = 4.5 \times 10^{-12} J = 28 \text{ MeV} \quad \dots(10.34)$$

Corresponding Fermi temperature is

$$T_F = \frac{\epsilon_F}{k} = 3.26 \times 10^{11} \text{ K} \quad \dots(10.35)$$

This shows that the ideal neutron gas is degenerate.

## 10.6 FERMI ENERGY AS A FUNCTION OF TEMPERATURE

For a discussion of properties such as the specific heat or entropy, it is essential to consider the behaviour of the system at temperatures above absolute zero. We will, therefore, obtain the expression for the Fermi energy as a function of temperature.

In the study of this kind it is frequently necessary to evaluate integrals involving the Fermi function  $f(\epsilon)$ , i.e., integrals of the type

$$\int_0^\infty f(\epsilon) \phi(\epsilon) d\epsilon \quad \dots(10.36)$$

where the Fermi function  $1/(e^{\beta(\epsilon-\mu)} + 1)$  and  $\phi(\epsilon)$  are smoothly varying functions of  $\epsilon$

Integrating by parts

$$I = \left[ \pm f(\epsilon) \int_0^\epsilon \phi(\epsilon) d\epsilon \right]_0^\infty - \int_0^\infty \psi(\epsilon) f'(\epsilon) d\epsilon \quad \dots(10.37)$$

where

$$\psi(\epsilon) = \int_0^\epsilon \phi(\epsilon) d\epsilon \quad \dots(10.38)$$

Now

$$f(\infty) = \frac{1}{e^\infty + 1} = 0$$

and

$$\psi(0) = \int_0^0 \phi(\epsilon) d\epsilon = 0$$

Therefore, the first term in Eq. (10.37) vanishes at both the limits.

Hence

$$I = - \int_0^\infty \psi(\epsilon) f'(\epsilon) d\epsilon \quad \dots(10.39)$$

Since, in all practical cases, the temperature is small compared with Fermi temperature of the gas, the differential  $f'(\epsilon)$  will be negligible except in the neighbourhood of the Fermi energy  $\epsilon_F$ . The form of  $f'(\epsilon)$  as a function of  $\epsilon$  is shown in Fig. 10.2.

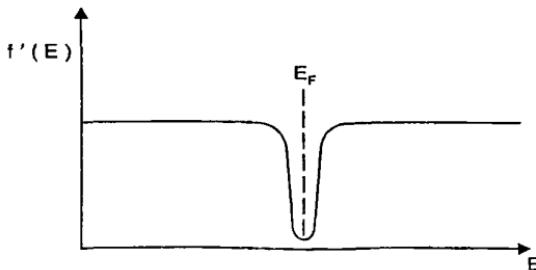


Fig. 10.2

Only a relatively narrow range, about  $\epsilon = \epsilon_F$ , contributes appreciably to the integral. Let us, therefore, expand  $\psi(\epsilon)$  about  $\epsilon_F$  in a power series:

$$\psi(\epsilon) = \psi(\epsilon_F) + \psi'(\epsilon_F)(\epsilon - \epsilon_F) + \psi''(\epsilon_F) \frac{(\epsilon - \epsilon_F)^2}{2!} + \dots \quad \dots(10.40)$$

Therefore

$$I = - \int_0^\infty \psi(\epsilon_F) f'(\epsilon) d\epsilon - \int_0^\infty \psi'(\epsilon_F)(\epsilon - \epsilon_F) f'(\epsilon) d\epsilon - \int_0^\infty \psi''(\epsilon_F) \frac{(\epsilon - \epsilon_F)^2}{2} f'(\epsilon) d\epsilon \quad \dots(10.41)$$

$= -I_1 - I_2 - I_3$ , neglecting the higher terms  
...(10.42)

Now  $I_1 = \int_0^{\infty} \psi(\varepsilon_F) f'(\varepsilon) d\varepsilon = \psi(\varepsilon_F) \int_0^{\infty} f'(\varepsilon) d\varepsilon$   
 $= \psi(\varepsilon_F) [f(\varepsilon)]_0^{\infty} = -\psi(\varepsilon_F) \cdot \frac{1}{e^{-\varepsilon_F/kT} + 1}$

and, because  $\varepsilon_F > > kT$ ,

$$I_1 = -\psi(\varepsilon_F) = - \int_0^{\varepsilon_F} \varphi(\varepsilon) d\varepsilon \quad \dots(10.43)$$

$$I_2 = \int_0^{\infty} \psi'(\varepsilon_F) (\varepsilon - \varepsilon_F) f'(\varepsilon) d\varepsilon \quad \dots(10.44)$$

$$= -\psi'(\varepsilon_F) \int_0^{\infty} \frac{(\varepsilon - \varepsilon_F) e^{\frac{\varepsilon - \varepsilon_F}{kT}}}{kT \left( e^{\frac{\varepsilon - \varepsilon_F}{kT}} + 1 \right)^2} d\varepsilon$$

Putting  $x = \frac{\varepsilon - \varepsilon_F}{kT}$

$$I_2 = \psi'(\varepsilon_F) kT \int_{\frac{\varepsilon_F}{kT}}^{\infty} \frac{x e^x}{\left[ e^x + 1 \right]^2} dx \quad \dots(10.45)$$

Because  $\varepsilon_F \gg kT$  and  $e^{-x}$  is a rapidly decreasing function of  $x$ , the lower limit  $\frac{\varepsilon_F}{kT}$  may be replaced by  $-\infty$ .

Therefore  $I_2 = \psi'(\varepsilon_F) kT \int_{-\infty}^{\infty} \frac{x e^x}{\left[ e^x + 1 \right]^2} dx \quad \dots(10.46)$

The integrand being an odd function, the definite integral changes sign if  $x$  is replaced by  $-x$ . Therefore, the integral is zero.

Hence,  $I_2 = 0 \quad \dots(10.47)$

$$I_3 = \int_0^{\infty} \psi''(\varepsilon_F) \frac{(\varepsilon - \varepsilon_F)^2}{2} f'(\varepsilon) d\varepsilon$$

$$= -\frac{\psi''(\varepsilon_F)}{2} (kT)^2 \int_{-\infty}^{\infty} \frac{x^2 e^x}{\left[ e^x + 1 \right]^2} dx \quad \dots(10.48)$$

In this case, the integrand is an even function of  $x$ .

Therefore,

$$\begin{aligned} I_3 &= -\psi'(\varepsilon_F)(kT)^2 \int_0^{\infty} \frac{x^2 e^x}{[e^x + 1]^2} dx \\ &= -\psi'(\varepsilon_F)(kT)^2 \int_0^{\infty} \frac{x^2 e^{-x}}{[e^{-x} + 1]^2} dx \end{aligned} \quad \dots(10.49)$$

Now

$$\begin{aligned} [1 + e^{-x}]^{-2} &= 1 - 2e^{-x} + 3e^{-2x} - 4e^{-3x} + \dots \\ &= \sum_{n=1}^{\infty} (-1)^{n-1} n e^{-(n-1)x} \end{aligned} \quad \dots(10.50)$$

$$\text{Therefore, } \int_0^{\infty} \frac{x^2 e^{-x}}{[1 + e^{-x}]^2} dx = \int_0^{\infty} \sum_{n=1}^{\infty} (-1)^{n-1} n x^2 e^{-nx} dx$$

$$\begin{aligned} &= \sum_{n=1}^{\infty} (-1)^{n-1} n \int_0^{\infty} x^2 e^{-nx} dx \\ &= \sum_{n=1}^{\infty} (-1)^{n-1} n \frac{2}{n^3} = 2 \sum_{n=1}^{\infty} (-1)^{n-1} \frac{1}{n^2} \\ &= \sum_{n=1}^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6} \end{aligned} \quad \dots(10.51)$$

$$\text{Therefore } I_3 = -\psi'(\varepsilon_F)(kT)^2 \frac{\pi^2}{6} = \varphi'(\varepsilon_F)(kT)^2 \frac{\pi^2}{6} \quad \dots(10.52)$$

(because by Eq. (10.38)  $\psi'(\varepsilon) = \varphi(\varepsilon)$  and  $\psi^{11}(\varepsilon) = \varphi'(\varepsilon)$ )

Hence

$$\begin{aligned} I &= -I_1 - I_3 \\ &= \int_0^{\varepsilon_F} [\varphi(\varepsilon) + \varphi'(\varepsilon_F)(kT)^2] \frac{\pi^2}{6} d\varepsilon \end{aligned} \quad \dots(10.53)$$

Let us use this equation to evaluate the Fermi energy at temperature  $T$ . We know that

$$N = \int_0^{\infty} f(\varepsilon) \sigma(\varepsilon) d\varepsilon \quad \dots(10.54)$$

Using Eq. (10.53) and replacing  $\varphi(\varepsilon)$  by  $\sigma(\varepsilon)$ , we get

$$N = \int_0^{\varepsilon_F} \sigma(\varepsilon) d\varepsilon + \sigma'(\varepsilon_F)(kT)^2 \frac{\pi^2}{6} \quad \dots(10.55)$$

We may recall that

$$N = \int_0^{\epsilon_F(0)} \sigma(\epsilon) d\epsilon \quad \dots(10.56)$$

where  $\epsilon_F(0)$  is the Fermi energy at  $T = 0$  K.

$$\begin{aligned} \text{Therefore, } \sigma'(\epsilon_F)(kT)^2 \frac{\pi^2}{6} &= \int_0^{\epsilon_F(0)} \sigma(\epsilon) d\epsilon - \int_0^{\epsilon_F} \sigma(\epsilon) d\epsilon \\ &= \int_{\epsilon_F}^{\epsilon_F(0)} \sigma(\epsilon) d\epsilon \end{aligned} \quad \dots(10.57)$$

Since the Fermi energy  $\epsilon_F$  differs only slightly from its value  $\epsilon_F(0)$  at 0 K, we may write

$$\int_{\epsilon_F}^{\epsilon_F(0)} \sigma(\epsilon) d\epsilon = \sigma(\epsilon_F(0)) (\epsilon_F(0) - \epsilon_F) \quad \dots(10.58)$$

$$\text{Therefore, } \sigma'(\epsilon_F)(kT)^2 \frac{\pi^2}{6} = \sigma(\epsilon_F(0)) (\epsilon_F(0) - \epsilon_F) \quad \dots(10.59)$$

Since by Eq. (10.10)

$$\begin{aligned} \sigma(\epsilon_F) &= \frac{V(2m)^{3/2} \epsilon^{1/2}}{4\pi^2 \hbar^3} \\ \sigma'(\epsilon_F) &= \frac{V(2m)^{3/2}}{4\pi^2 \hbar^3 \epsilon^{1/2}} = \frac{\sigma(\epsilon)}{2\epsilon} \end{aligned} \quad \dots(10.60)$$

Therefore, Eq. (10.59) changes to

$$\frac{\sigma(\epsilon_F)}{2\epsilon_F}(kT)^2 \frac{\pi^2}{6} = \sigma(\epsilon_F(0))(\epsilon_F(0) - \epsilon_F) \quad \dots(10.61)$$

Further, because  $\epsilon_F \approx \epsilon_F(0)$

$$\frac{\sigma(\epsilon_F)}{\epsilon_F} = \frac{\sigma(\epsilon_F(0))}{\epsilon_F(0)}$$

$$\text{and } \frac{\sigma(\epsilon_F(0))}{2\epsilon_F(0)}(kT)^2 \frac{\pi^2}{6} = \sigma(\epsilon_F(0))(\epsilon_F(0) - \epsilon_F) \quad \dots(10.62)$$

$$\text{i.e. } \frac{(kT)^2}{\epsilon_F(0)} \frac{\pi^2}{12} = \epsilon_F(0) - \epsilon_F \quad \dots(10.63)$$

$$\text{Hence } \epsilon_F = \epsilon_F(0) \left( 1 - \frac{(kT)^2}{(\epsilon_F(0))^2} \frac{\pi^2}{12} \right) \quad \dots(10.64)$$

$$= \epsilon_F(0) \left\{ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 \right\} \quad \dots(10.65)$$

Thus, we see that the Fermi level is lowered by increasing temperature.

## 10.7 ELECTRONIC SPECIFIC HEAT

Total energy  $E$  is given by

$$E = \int_0^{\infty} \epsilon f(\epsilon) \sigma(\epsilon) d\epsilon \quad \dots(10.66)$$

The integral can be evaluated using Eq. (10.53). In this equation, we replace  $\varphi(\epsilon)$  by  $\epsilon \sigma(\epsilon)$ . We get

$$E = \int_0^{\epsilon_F} \epsilon \sigma(\epsilon) d\epsilon + \sigma(\epsilon_F)(kT)^2 \frac{\pi^2}{6} + \epsilon_F \sigma'(\epsilon_F)(kT)^2 \frac{\pi^2}{6} \quad \dots(10.67)$$

As in the preceding section

$$\begin{aligned} \int_0^{\epsilon_F} \epsilon \sigma(\epsilon) d\epsilon &= \int_0^{\epsilon_F(0)} \epsilon \sigma(\epsilon) d\epsilon - \int_{\epsilon_F}^{\epsilon_F(0)} \epsilon \sigma(\epsilon) d\epsilon \\ &= E_0 - \epsilon_F(0) \sigma(\epsilon_F(0)) (\epsilon_F(0) - \epsilon_F) \end{aligned} \quad \dots(10.68)$$

where  $E_0 = \int_0^{\epsilon_F(0)} \epsilon \sigma(\epsilon) d\epsilon$  is the total energy of the electrons at  $T = 0$  K.

By Eq. (10.63)

$$\epsilon_F(0) - \epsilon_F = \frac{(kT)^2}{\epsilon_F(0)} \frac{\pi^2}{12}$$

$$\text{Therefore } \int_0^{\epsilon_F} \epsilon \sigma(\epsilon) d\epsilon = E_0 - \sigma(\epsilon_F(0)) (kT)^2 \frac{\pi^2}{12} \quad \dots(10.69)$$

The last two terms of Eq. (10.67) can be expressed as

$$\begin{aligned} &\{\sigma(\epsilon_F) + \epsilon_F \sigma'(\epsilon_F)\} (kT)^2 \frac{\pi^2}{6} \\ &= \left\{ \sigma(\epsilon_F) + \sigma \frac{(\epsilon_F)}{2} \right\} (kT)^2 \frac{\pi^2}{6} \quad [\text{see Eq. (10.60)}] \\ &= \frac{3}{2} \sigma(\epsilon_F) (kT)^2 \frac{\pi^2}{6} \approx \frac{3}{2} \sigma(\epsilon_F(0)) (kT)^2 \frac{\pi^2}{6} \end{aligned} \quad \dots(10.70)$$

$$\text{Therefore } E = E_0 - \sigma(\epsilon_F(0)) (kT)^2 \frac{\pi^2}{12} + \frac{3}{2} \sigma(\epsilon_F(0)) (kT)^2 \frac{\pi^2}{6}$$

$$= E_0 + \sigma(\epsilon_F(0)) (kT)^2 \frac{\pi^2}{6} \quad \dots(10.71)$$

Now

$$E_0 = \frac{3}{5} N \epsilon_F(0) \quad [\text{See Eq. (10.26)}]$$

and

$$N = \int_0^{\epsilon_F(0)} \sigma(\epsilon) d\epsilon \quad [\text{See Eq. (10.09)}]$$

$$\begin{aligned} &= \frac{V}{2\pi^2 \hbar^3} (2m)^{3/2} \int_0^{\epsilon_F(0)} \epsilon^{1/2} d\epsilon \\ &= \frac{2}{3} \frac{V}{2\pi^2 \hbar^2} (2m)^{3/2} [\epsilon_F(0)]^{3/2} \\ &= \frac{2}{3} \cdot \epsilon_F(0) \sigma(\epsilon_F(0)) \end{aligned} \quad \dots(10.72)$$

or

$$\sigma(\epsilon_F(0)) = \frac{3N}{2\epsilon_F(0)} \quad \dots(10.73)$$

Hence

$$\begin{aligned} E &= \frac{3}{5} N \epsilon_F(0) + \frac{3N}{2\epsilon_F(0)} (kT)^2 \frac{\pi^2}{6} \\ &= N \left\{ \frac{3}{5} \epsilon_F(0) + \frac{(kT)^2 \pi^2}{4\epsilon_F(0)} \right\} \end{aligned} \quad \dots(10.74)$$

Therefore, the mean energy of an electron

$$\langle \epsilon \rangle = \frac{E}{N} = \frac{3}{5} \epsilon_F(0) + \frac{(kT)^2 \pi^2}{4\epsilon_F(0)} \quad \dots(10.75)$$

$$= \epsilon_F(0) \left\{ \frac{3}{5} + \frac{\pi^2 T^2}{4 T_F^2} \right\} \quad \dots(10.76)$$

The electronic specific heat  $C_V$  is

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{N k^2 \pi^2 T}{2\epsilon_F(0)} = \frac{\pi^2}{2} R \frac{T}{T_F} \quad \dots(10.77)$$

Specific heat  $C_V$ , therefore, varies linearly with temperature and vanishes at  $T = 0$  in conformity with the third law of thermodynamics.

In order to have an idea of the magnitude of the electronic contribution to the specific heat at room temperature, let us suppose that the Fermi temperature is  $T = 45000 K$  (note that Fermi temperature is invariably of the order of  $10^4$  to  $10^5 K$ ).

$$\text{Therefore } C_V = \frac{\pi^2}{2} R \frac{300}{45000} = 0.03 R \quad \dots(10.78)$$

This is very small compared to the lattice contribution :  $3R$ . The electronic specific heat, therefore, is not normally detected at room temperature.

In general, the low-temperature specific heat of a metal is given by

$$C_V = \gamma T + \delta T^3 \quad \dots(10.79)$$

$$= \frac{\pi^2 N k^2}{2 \epsilon_F(0)} T + \frac{12 \pi^4 N k}{5 \theta_D^3} T^3 \quad [\text{See Eq. (9.77)}] \\ \dots(10.80)$$

A plot of  $C_V/T$  against  $T^2$ , therefore, should give a straight line. Experimental measurements of the specific heat of copper, silver, etc., in the temperature range 1 – 5 K have amply justified this expectation. The slope of the line gives the coefficient  $\delta$  which enables us to evaluate the Debye temperature  $\theta_D$ ; while the intercept on the  $C_V/T$  axis gives  $\gamma$  which yields the value of  $\epsilon_F$ .

Now, pressure

$$P = \frac{2 E}{3 V} \\ = \frac{2}{3} \frac{N}{V} \left\{ \frac{3}{5} \epsilon_F(0) + \frac{(kT)^2 \pi^2}{4 \epsilon_F(0)} \right\} \\ = \frac{2}{5} n \epsilon_F(0) \left\{ 1 + \frac{5}{12} \frac{(kT)^2 \pi^2}{(\epsilon_F(0))^2} \right\} \quad \dots(10.81)$$

This shows that even at absolute zero, the pressure does not vanish. This is a consequence of Pauli exclusion principle, which allows only one particle to have zero momentum. Other particles having finite momentum give rise to the zero point pressure.

## 10.8 WHITE DWARFS

In this section we shall illustrate an application of the degenerate electron gas theory to a problem in stellar structure.

White dwarf stars occupy a key position in astrophysical theory. Their properties provide clues to the physical processes, that take place during the evolutionary states near the ends of stellar lifetimes. Important contributions to our understanding of these stars have come from statistical mechanics.

If a plot is made of the brightness of stars against the predominant wavelength emitted, as shown in Fig. 10.3, it will be found that most of the stars fall within a linear strip, indicating that the brightness is proportional to  $\lambda$ . Such a plot is known as the Hertzsprung-Russel diagram. The sequence of stars is called the 'main sequence'. There are however, two glaring exceptions to this general rule:

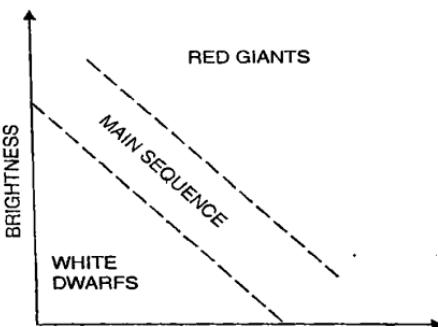


Fig. 10.3

(i) the red giant stars which are huge and abnormally bright and (ii) the white dwarf stars which are 'highly underluminous'. The companion of Sirius which is a white dwarf, has a mass almost equal to that of the sun, but its luminosity is only 0.003 times that of the sun.

It is now known that hydrogen is the most abundant element in the universe and that it makes up about 70 per cent of the mass of ordinary stars. Bethe (1938), from his calculations of the rates of thermonuclear reactions involving hydrogen conditions appropriate to stellar interiors, indicated that these reactions provide the energy source necessary for the stars to derive their luminosities. Application of Bethe's results to white dwarf showed that they have exhausted their thermonuclear energy sources and are among the terminal states of stellar evolution. One has to account, however, for the source of energy they will still radiate. This was done by Mestel in 1952, who pointed out that the thermal energy content of the hot white-dwarf interior, leaking slowly away through the insulating surface layers, is entirely sufficient to explain the observed luminosities.

White dwarfs have stellar masses but much smaller diameters and, hence, are very dense. The gravitational red-shift of light predicted by Einstein's general theory of relativity and measured in the white dwarf Sirius B (one of the first white dwarfs to be discovered) confirmed the small size and high density of this star. Some of the properties of Sirius B are given in Table 10.1. For comparison the corresponding values for the sun are also given.

Table 10.1  
Physical constants of Sirius B and the Sun\*

Quantity	Sirius B	Sun
1. Mass	$1.05 MO$	$MO = 1.989 \times 10^{20} \text{ Kg}$
2. Radius	$0.008 RO$	$RO = 6.96 \times 10^8 \text{ m}$
3. Electron temperature	$27000 \text{ K}$	$5800 \text{ K}$
4. Gravitational red shift	$89 \pm 16 \text{ km/sec}$	$0.6 \text{ km/sec}$
5. Mean density	$2.8 \times 10^9 \text{ kg/m}^3$	$1.41 \times 10^3 \text{ kg/m}^3$
6. Central density	$3.3 \times 10^9 \text{ kg/m}^3$	$1.6 \times 10^5 \text{ kg/m}^3$
7. Central temperature	$2.2 \times 10^7 \text{ K}$	$1.6 \times 10^7 \text{ K}$

Note that the radius of the earth,  $6.37 \times 10^6 \text{ m} = 0.009 R$ , is larger than that of Sirius B. Existence of such compact stars could not be satisfactorily explained until the quantum-statistical theory of the electron gas was worked out by Fermi and Dirac. It has been shown by R.H. Fowler and S. Chandrasekhar that such stellar configurations can satisfactorily be described by treating the electrons within the stars as a completely degenerate relativistic Fermi gas. Chandrasekhar found that there is a critical stellar mass above which stable degenerate dwarfs cannot exist.

From some typical data for such a star an idealized model for a white dwarf may be constructed.

Imagine a star with

$$\text{mass } M = 10^{30} \text{ kg}$$

$$\text{density } \rho = 10^{10} \text{ kg/m}^3$$

and central temperature  $T = 10^7 \text{ K}$  (see Table 10.1)

Material content of white dwarf is mostly helium and the temperature  $10^7 \text{ K}$  corresponds to a mean thermal energy of 1000 eV, which is much larger in comparison with the energy required for ionizing a helium atom. Hence, the helium atoms in the star are expected to be in a state of complete ionization and the star may be regarded as a gas composed of  $N$  electrons and  $N/2$  helium nuclei. Therefore, the mass of the star is given by

$$M = N(m + 2m_p) \approx 2N m_p \quad \dots(10.82)$$

where  $m$  is the mass of an electron and  $m_p$  the mass of a proton

Mass of helium nuclei  $\approx 4m_p$

The electron density, therefore, is

$$n = \frac{N}{V} = \frac{M/2m_p}{M/\rho} = \frac{\rho}{2m_p} \approx 10^{36} \text{ electrons/m}^3$$

\* Hugh M. van Horn. *Physics Today*, 32, 25, 1979.

Substituting this value for  $N/V$  in the expression (10.13) for  $\epsilon_F$  we can calculate  $T_F$  from the relation (10.30), viz.  $T_F = \frac{\epsilon_F}{k}$  which comes out to be of the order of  $10^{10}$  K. Since this is much higher than the temperature of the star, the electron gas must be a highly degenerate Fermi gas. Fermi energy is of the order of 1 MeV, which is comparable with the rest energy  $mc^2$  of the electron and, therefore, the dynamics of the electrons is relativistic. Though helium nuclei do not contribute significantly to the dynamics of the problem and, hence, may be neglected, they do provide the gravitational attraction to hold the entire system together.

Let us now consider the equilibrium configuration of our idealized model.

At the centre of a star, the temperature is very high – of the order of  $10^7$  K – and the atoms there are completely ionized. In young stars, the pressure due to the thermal motion of the electrons and ions near the centre is sufficient to withstand the weight of the material above it and prevent the gravitational collapse of the star. In white dwarfs, the gravitational collapse of the core is prevented by the pressure of a degenerate electron gas.

Assuming the configuration to be spherical, the gas will exert a pressure  $P_0(r)$  on the boundary of the sphere and any expansion will involve the expenditure of work. An adiabatic change in volume will cause a change  $dE_0$  in energy given by

$$\begin{aligned} dE_0 &= -P_0(r) dV \\ &= -P_0(r) 4\pi r^2 dr \end{aligned} \quad \dots(10.83)$$

If these were the only forces present, the system would expand indefinitely. However, there is gravitational interaction and, therefore, there is a change in the gravitational self-energy as well.

Gravitational self-energy can be calculated as follows:

Consider a sphere of uniform mass density  $\rho$  and radius  $r$  (Fig. 10.4). The mass of the sphere is  $\frac{4}{3}\pi r^3 \rho$ . The work done in bringing an extra shell of thickness  $dr$  is

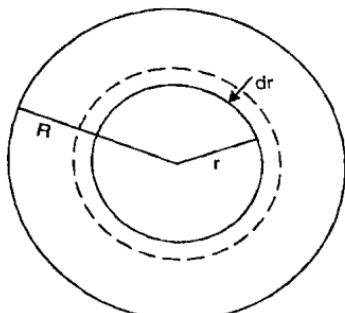


Fig. 10.4

$$\begin{aligned} W &= - \int_0^R G \frac{4}{3} \pi r^3 \rho \times \frac{4\pi r^2 \rho dr}{r} \\ &= - \frac{16}{3} G \pi^2 \rho^2 \int_0^R r^4 dr \\ &= - \frac{16}{3} G \pi^2 \rho^2 \times \frac{R^5}{5} \\ &= - \frac{3}{5} \frac{T}{R} \left( \frac{4}{3} \pi R^3 \rho \right)^2 = - \frac{3}{5} \frac{GM^2}{R} \end{aligned} \quad \dots(10.84)$$

If the configuration is in equilibrium, the change in its energy for an infinitesimal change in its size must be identically zero, i.e.

$$-p_0(r)4\pi r^2 + \frac{\frac{3}{5}GM^2}{r^2} = 0$$

or  $p_0(r) = \frac{3GM^2}{20r^2}$  ... (10.85)

It is evident that to find the relation between  $M$  and  $r$  we have to find the value of  $p_0(r)$  which we will now proceed to find.

The single-particle energy of a relativistic particle is given by

$$E = \sqrt{p^2c^2 + m^2c^4} \quad \dots (10.86)$$

The ground state energy of the Fermi gas, therefore, is

$$\begin{aligned} E_0 &= 2 \sum \sqrt{p^2c^2 + m^2c^4} \\ &= \frac{V}{\pi^2\hbar^2} \int_0^{p_F} p^2 \sqrt{p^2c^2 + m^2c^4} dp \end{aligned} \quad \dots (10.87)$$

where the factor 2 accounts for the spin degeneracy and  $p_F$  is the Fermi momentum.

$$p_F = \hbar \left( \frac{3N\pi^2}{V} \right)^{1/3}$$

Put  $x = p/mc$

$$\begin{aligned} \text{Therefore } E_0 &= \frac{Vm^4c^5}{\pi^2\hbar^3} \int_0^{x_F} x^2 \sqrt{x^2 + 1} dx \\ &= \frac{V}{\pi^2\hbar^3} m^4 c^5 f(x_F) \end{aligned} \quad \dots (10.88)$$

$$\text{where } f(x_F) = \int_0^{x_F} x^2 \sqrt{x^2 + 1} dx$$

$$\text{and } x_F = \frac{p_F}{mc} = \frac{\hbar}{mc} \left( \frac{3\pi^2 N}{V} \right)^{1/3} \quad \dots (10.90)$$

$$\text{Since } \frac{N}{V} = \frac{M/2m_p}{\frac{4}{3}\pi R^3} = \frac{3M}{8\pi m_p R^3} \quad \dots (10.91)$$

$$x_F = \frac{\hbar}{mc} \left( \frac{3\pi^2 3M}{8\pi m_p R^3} \right)^{1/3} = \left( \frac{9\pi M \hbar^3}{8m^3 c^3 m_p R^3} \right)^{1/3} \quad \dots (10.92)$$

The pressure exerted by the Fermi gas

$$p_0 = -\frac{\partial E_0}{\partial V} \quad \dots(10.93)$$

$$\begin{aligned} &= -\frac{m^4 c^5}{\pi^2 \hbar^3} f(x_F) - \frac{m^4 c^5 V}{\pi^2 \hbar^3} \cdot \frac{\partial f(x_F)}{\partial x_F} \frac{\partial x_F}{\partial V} \\ &= -\frac{m^4 c^5}{\pi^2 \hbar^3} f(x_F) + \frac{m^4 c^5}{3\pi^2 \hbar^2} x_F^3 \sqrt{1+x_F^2} \end{aligned}$$

[by Eq. (10.91)]

$$\text{or } p_0 = \frac{m^4 c^5}{\pi^2 \hbar^3} \left[ \frac{1}{3} x_F^3 \sqrt{1+x_F^2} - f(x_F) \right]; \quad \dots(10.94)$$

(i) If  $x_F \ll 1$ , i.e.  $\frac{p_F}{mc} \ll 1$  we would be dealing with a non-relativistic case.

$$\begin{aligned} \text{Therefore } \int_0^{x_F} x^2 \sqrt{1+x^2} dx &= \int_0^{x_F} \left( x^2 + \frac{1}{2} x^4 + \dots \right) dx \\ &\approx \frac{x_F^3}{3} + \frac{x_F^5}{10} \end{aligned} \quad \dots(10.95)$$

$$\text{and } \frac{1}{3} x_F^3 \sqrt{1+x_F^2} \approx \frac{x_F^3}{3} + \frac{x_F^5}{6} \quad \dots(10.96)$$

where higher terms are neglected.

Substituting Eqs. (10.95) and (10.96), in Eq. (10.94)

$$P_0 = \frac{m^4 c^5}{15\pi^2 \hbar^3} = \frac{m^4 c^5}{15\pi^2 \hbar^3} \left( \frac{9\pi M \hbar^3}{8m^3 c^3 m_p R^3} \right)^{5/3} \quad \dots(10.97)$$

Therefore from Eq. (10.85)

$$\frac{m^4 c^5}{15\pi^2 \hbar^3} \left( \frac{9\pi M \hbar^3}{8m^3 c^3 m_p R^3} \right)^{5/3} = \frac{3GM^2}{20\pi R^4} \quad \dots(10.98)$$

$$\text{Hence } M^{1/3} R = \frac{4\hbar^2}{9mG\pi} \left( \frac{9\pi}{8m_p} \right)^{5/3} \quad \dots(10.99)$$

(ii) If, on the other hand,  $x_F \gg 1$  the case is extreme relativistic. In this case

$$f(x_F) = \int_0^{x_F} x^2 \sqrt{1+x^2} dx = \int_0^{x_F} x^2 \left( x + \frac{1}{2x} + \dots \right) dx$$

$$\approx \frac{x_F^4}{4} + \frac{x_F^2}{4} \quad \dots(10.100)$$

and  $\frac{1}{3}x_F^3\sqrt{x_F^2+1} = \frac{x_F^4}{3} + \frac{x_F^2}{6}$   $\dots(10.101)$

Therefore  $P_0 \approx \frac{m^4 c^5}{\pi^2 \hbar^3} \left[ \frac{x_F^4}{3} + \frac{x_F^2}{6} + \frac{x_F^4}{4} + \frac{x_F^2}{4} \right]$

$$\approx \frac{m^4 c^5}{12\pi^2 \hbar^3} (x_F^4 - x_F^2) \quad \dots(10.102)$$

Therefore, from Eq. (10.85)

$$\frac{m^4 c^5}{12\pi^2 \hbar^3} (x_F^4 - x_F^2) = \frac{3G^2}{20\pi R^4} \quad \dots(10.103)$$

or  $\frac{m^4 c^5}{12\pi^2 \hbar^3} x_F^2 (x_F^2 - 1) = \frac{3GM^2}{20\pi R^4} \quad \dots(10.104)$

Therefore  $\frac{m^4 c^5}{12\pi^2 \hbar^3} \left( \frac{9\pi \hbar^3}{8m^3 c^3 m_p} \right)^{2/3} \frac{M^{2/3}}{R^2} \left\{ \left( \frac{9\pi \hbar^3}{8m^3 c^3 m_p} \right)^{2/3} \frac{M^{2/3}}{R^2} \right\}$   
 $= \frac{3GM^2}{20\pi R^4} \quad \dots(10.105)$

For convenience, let us put

$$X = \frac{m^4 c^5}{12\pi^2 \hbar^3} \text{ and } Y = \left( \frac{9\pi \hbar^3}{8m^3 c^3 m_p} \right)^{2/3}$$

Eq. (10.105) can now be written as

$$XY \left( Y \frac{M^{2/3}}{R^2} - 1 \right) = \frac{3GM^2}{20\pi R^4} \quad \dots(10.106)$$

Therefore  $\frac{1}{R^2} \left( YM^{2/3} - \frac{3G}{20\pi XY} M^{4/3} \right) = 1 \quad \dots(10.107)$

and, hence,  $R = M^{1/3} \left( Y - \frac{3G}{20\pi XY} M^{2/3} \right)^{1/2} \quad \dots(10.108)$

Now  $R$  must be positive or zero.

Therefore  $Y > \frac{3G}{20\pi XY} M^{2/3}$

i.e.  $M^{2/3} < \frac{20\pi XY^2}{3G} \quad \dots(10.109)$

or

$$M < \left( \frac{20\pi XY^2}{3G} \right)^{3/2} \quad \dots(10.110)$$

Therefore  $M_{ch} = \left( \frac{20\pi XY^2}{3G} \right)^{3/2} = \left( \frac{5m^4 c^5}{9G\pi\hbar^3} \right)^{3/2} \left( \frac{9\pi\hbar^3}{8m^3 c^3 m_p} \right) \quad \dots(10.111)$

is the limiting mass.  $M_{ch}$  is known as the 'Chandrasekhar limit'. This limit as calculated from Eq. (10.111) comes out to be equal to  $3.40 \times 10^{30}$  kg. Since the mass of the sun is  $M_s = 1.99 \times 10^{30}$  kg, the critical mass of white dwarfs is  $1.7 M_s$ . Detailed investigations of Chandrasekhar lead to the result  $M_{ch} = 1.44 M_s$ , where  $M_s$  is the mass of the sun. This was a major discovery and has profound consequences for the final stages of stellar evolution. Stars that end their evolution with masses in excess of this limit have gravitational self-attraction too great to be counter-balanced by the pressure of the degenerate electrons and are doomed to ultimate collapse.

## 10.9 COMPRESSIBILITY OF FERMI GAS

Let us derive an expression for the compressibility of a Fermi gas at absolute zero.

The energy at absolute zero is

$$E_0 = \int_0^{\epsilon_F} \epsilon \sigma(\epsilon) d\epsilon = \frac{V(2m)^{3/2}}{2\pi^2 \hbar^3} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon \quad \dots(10.112)$$

$$= \frac{V(2m)^{3/2}}{2\pi^2 \hbar^3} \cdot \frac{2}{5} \epsilon_F^{5/2} \quad \dots(10.113)$$

Hence  $P_0 = \frac{2}{3} \frac{E_0}{V} = \frac{2(2m)^{3/2}}{15\pi^2 \hbar^3} \epsilon_F^{5/2} \quad \dots(10.114)$

$$\begin{aligned} &= \frac{2(2m)^{3/2}}{15\pi^2 \hbar^3} \cdot \frac{\hbar^5}{(2m)^{5/2}} \left( \frac{3N\pi^2}{V} \right)^{5/2} \\ &= \frac{3^{2/3} \hbar^2 \pi^{4/3}}{5m} \left( \frac{N}{V} \right)^{5/3} \quad \dots(10.115) \end{aligned}$$

Therefore  $\ln P_0 = \ln \left\{ \frac{3^{2/3} \hbar^2 \pi^{4/3} N^{5/3}}{5m} \right\} - \frac{5}{3} \ln V \quad \dots(10.116)$

Hence  $\frac{\partial \ln V}{\partial P_0} = -\frac{3}{5P_0}$

Therefore, the compressibility

$$\begin{aligned} -\frac{1}{V} \frac{\partial V}{\partial P_0} &= \frac{3}{5} \frac{5m}{3^{2/3} \hbar^2 \pi^{4/3}} \left( \frac{N}{V} \right)^{-5/3} \\ &= \frac{3^{1/3} m}{\hbar^2 \pi^{4/3}} \left( \frac{N}{V} \right)^{-5/3} \end{aligned} \quad \dots(10.117)$$

It has been found that the compressibility of alkali metals is close to the compressibility of an electron gas.

## 10.10 PAULI PARAMAGNETISM

According to Pauli, the paramagnetism of alkali metals can also be explained on the basis of the concept of a free electron gas. If we place a Fermi gas consisting of electrons in a magnetic field  $H$ , the energy of a particle,

(i) with spin parallel to  $H$  is  $\epsilon = \frac{p^2}{2m} - \mu H$  and (ii) with spin anti-parallel to  $H$  is

$$\epsilon = \frac{p^2}{2m} + \mu H \quad \dots(10.118)$$

where  $\mu$  is the intrinsic magnetic moment of the particle.

At  $T = 0$ , all levels up to Fermi level  $\epsilon_F$  will be filled up. Therefore, the kinetic energy of the first group will range from 0 to  $\epsilon_F + \mu H$  while that of the second group from 0 to  $\epsilon_F - \mu H$ . The particles in each group, therefore, will be

$$\begin{aligned} N^+ &= \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^{\epsilon_F + \mu H} \epsilon^{1/2} d\epsilon \\ &= \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \frac{2}{3} (\epsilon_F + \mu H)^{3/2} \\ &= \frac{V}{6\pi^2 \hbar^3} (2m)^{3/2} (\epsilon_F + \mu H)^{3/2} \end{aligned} \quad \dots(10.119)$$

$$\text{and } N^- = \frac{V}{6\pi^2 \hbar^3} (2m)^{3/2} (\epsilon_F - \mu H)^{3/2} \quad \dots(10.120)$$

Therefore, the net magnetic moment of the gas is

$$\begin{aligned} M &= \mu(N^+ - N^-) \\ &= \frac{\mu V (2m)^{3/2}}{6\pi^2 \hbar^3} \left\{ (\epsilon_F + \mu H)^{3/2} - (\epsilon_F - \mu H)^{3/2} \right\} \end{aligned}$$

If the field is low

$$\begin{aligned} M &= \frac{\mu V(2m)^{3/2}}{6\pi^2\hbar^3} \left\{ \varepsilon_F^{3/2} + \frac{3}{2}\varepsilon_F^{1/2}\mu H - \varepsilon_F^{3/2} + \frac{3}{2}\varepsilon_F^{1/2}\mu H \right\} \\ &= \frac{\mu V(2m)^{3/2}}{6\pi^2\hbar^3} \cdot 3\varepsilon_E^{1/2}H \end{aligned} \quad \dots(10.121)$$

Therefore, the susceptibility

$$\chi_0 = \frac{M}{VH} = \frac{\mu^2(2m)^{3/2}\varepsilon_F^{1/2}}{2\mu^2\hbar^3} \quad \dots(10.122)$$

Substituting for  $(2m)^{3/2}$  from Eq. (10.28)

$$\chi_0 = \frac{\mu^2\varepsilon_F^{1/2}}{2\pi^2\hbar^3} \cdot \frac{3\hbar N\pi^2}{V\varepsilon_F^{3/2}} \quad \dots(10.123)$$

$$= \frac{3\mu^2 N}{2\varepsilon_F V} \quad \dots(10.123)$$

$$= \frac{3}{2} \frac{\mu^2 n}{\varepsilon_F} \quad \dots(10.124)$$

According to the Boltzmann treatment  $\chi$  is inversely proportional to  $T$  at high temperature and reaches a state of magnetic saturation at low temperatures. Pauli's treatment gives significantly different results. Equation (10.124) shows that the limiting susceptibility  $\chi_0$  is independent of temperature, but is strongly dependent upon the density of the gas. This is known as Pauli paramagnetism—in contrast the classical Langevin paramagnetism.

## 10.11 A RELATIVISTIC DEGENERATE ELECTRON GAS

In a completely degenerate extreme relativistic electron gas, the energy of a particle is given by

$$\varepsilon = cp \quad \dots(10.125)$$

Therefore

$$\varepsilon_F = cp_F = c\hbar \left\{ \frac{6\pi^2 N}{(2s+1)V} \right\}^{1/3} \quad \dots(10.126)$$

The total energy of the gas at absolute zero of temperature is

$$\begin{aligned} E_0 &= \frac{(2S+1)V}{2\pi^2\hbar^3} \int_0^{p_F} cp^3 dp \\ &= \frac{(2S+1)}{2\pi^2\hbar^3} \frac{cp_F^4}{4} \end{aligned}$$

$$= \frac{(2S+1)Vc\hbar}{8\pi^2} \left\{ \frac{6N\pi^2}{(2s+1)V} \right\}^{4/3}$$

$$= \frac{2c\hbar N\pi^{2/3}}{(2s+1)^{1/3}} \left( \frac{3}{4} \right)^{4/3} \left( \frac{N}{V} \right)^{1/3} \quad \dots(10.127)$$

$$P = -\frac{\partial E_0}{\partial V} = \frac{2c\hbar N^{4/3}\pi^{2/3}}{(2s+1)^{1/3}V^{4/3}} \cdot \frac{3^{1/3}}{4^{4/3}}$$

$$= 2c\hbar \left\{ \frac{3\pi^2}{2s+1} \right\}^{1/3} \cdot \left( \frac{N}{4V} \right)^{1/3} \quad \dots(10.128)$$

The pressure of an extreme relativistic gas is, therefore, proportional to  $N^{4/3}$ . Equations (10.127) and (10.128) lead to the relation

$$PV = \frac{1}{2} E \quad \dots(10.129)$$

It may be mentioned here that this relation is valid not only at absolute zero but at all temperatures.

## PROBLEMS

- 10.1** The density of sodium is  $0.97 \times 10^3 \text{ kg/m}^3$  and its molar mass is 0.023. Find the Fermi energy of the electron gas in metallic sodium and the specific heat of sodium at a temperature  $T$ .

- 10.2** Find the ratio of the mean velocity of an electron gas in an electron at the absolute zero of temperature to its velocity at the Fermi energy.

- 10.3** Density of copper is  $8.9 \times 10^3 \text{ kg/m}^3$  and its molar mass is 0.063. Find the maximum velocity of free electrons in copper at  $T = 0 \text{ K}$ .

- 10.4** Prove that (i)  $P - \frac{NkT}{V} \leq 0$  for BE gas

and (ii)  $P - \frac{NkT}{V} \geq 0$  for FD gas

- 10.5** Show that the Helmholtz free energy of a system of fermions is given by

$$F = \frac{3}{5} N \varepsilon_F^{(0)} \left[ 1 - \frac{5\pi^2}{12} \left( \frac{kT}{\varepsilon_F(0)} \right)^2 + \dots \right]$$

- 10.6** By what factor does the entropy of the conduction electrons change when the temperature is changed from 200 to 600 K?

- 10.7 Calculate the pressure exerted by the conduction electrons in silver metal on the solid lattice. Density of silver is  $10.5 \times 10^3 \text{ kg/m}^3$  and its molar mass is 0.108.
- 10.8 Estimate the numerical value of the low-temperature isothermal compressibility for the gas of conduction electrons in a potassium crystal. [Density =  $0.86 \times 10^3 \text{ kg/m}^3$ , Molar mass = 0.039].
- 10.9 Find the specific heat of a superdense electron gas, assuming the dependence of energy upon momentum to be extremely relativistic.
- 10.10 The energy and momentum of an electron in a relativistic completely degenerate gas are related by

$$\epsilon^2 = c^2 p^2 + m^2 c^4$$

Determine the equation of state of the gas.



# PHASE EQUILIBRIA

In this chapter we will be concerned with the systems comprising several phases in equilibrium with one another.

By a *phase* we mean a homogenous portion of a system which exhibits a macroscopic behaviour different from that of the other parts of the system and is separated from them by a well-defined boundary. Several phases of a system may co-exist in equilibrium with one another. Examples of two-phase systems are: a liquid and its saturated vapour, a liquid and a crystal, etc. In general, each phase may contain several components, e.g. several different species or molecules or ions. We shall restrict our discussion to the systems containing one component only. A one-component system can exist in different phases: gaseous, liquid or in a crystalline form. In a system whose phases are in equilibrium, a slight variation of external conditions results in a certain amount of the substance passing from one phase to another as can be observed, for example, in the fusion (*i.e.* condensation) or boiling of water. This process is known as *phase transition*. The study of the transition region between phases is one of the most interesting fields of statistical physics and, hence, while studying the conditions of phase equilibria, we will also consider the development of phase transitions. We shall describe the phase transitions in terms of macroscopic variables.

## 11.1 EQUILIBRIUM CONDITIONS

Let us first derive the conditions under which different phases can exist in equilibrium, so that no transfer of matter takes place from one phase to another.

Figure 11.1 shows a one-component system existing in two phases. The system is isolated from its surroundings and its energy is  $E$ , volume  $V$  and number of particles  $N$ . The corresponding quantities associated with the two phases are:  $E_1$ ,  $V_1$ ,  $N_1$  and  $E_2$ ,  $V_2$ ,  $N_2$  respectively.

$$E = E_1 + E_2; V = V_1 + V_2; N = N_1 + N_2 \quad \dots(11.1)$$

The entropy of the system is

$$\begin{aligned} S(E, V, N) &= S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \\ &= S_1(E_1, V_1, N_1) + S_2(E - E_1, V - V_1, N - N_1) \end{aligned} \quad \dots(11.2)$$

For equilibrium the entropy of the two systems must be maximum, i.e.  $dS = 0$ .

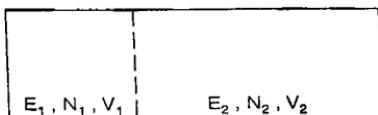


Fig. 11.1

$$\begin{aligned} \text{Therefore } dS &= \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left( \frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} dV_1 + \left( \frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} dN_1 \\ &\quad - \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2 - \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2} dV_2 - \left( \frac{\partial S_2}{\partial N_2} \right)_{E_2, V_2} dN_2 \\ &= \left[ \left( \frac{\partial S_1}{\partial E_1} \right) - \left( \frac{\partial S_2}{\partial E_2} \right) \right] dE_1 + \left[ \left( \frac{\partial S_1}{\partial V_1} \right) - \left( \frac{\partial S_2}{\partial V_2} \right) \right] dV_1 \\ &\quad + \left[ \left( \frac{\partial S_1}{\partial N_1} \right) - \left( \frac{\partial S_2}{\partial N_2} \right) \right] dN_1 = 0 \end{aligned} \quad \dots(11.3)$$

Since  $E_1, V_1, N_1$  are independent variables

$$\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} = 0 \quad \dots(11.4)$$

$$\frac{\partial S_1}{\partial V_1} - \frac{\partial S_2}{\partial V_2} = 0 \quad \dots(11.5)$$

$$\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} = 0 \quad \dots(11.6)$$

(1) We can see from Eq. (6.28) that

$$\frac{\partial S}{\partial E} = k\beta = \frac{1}{T} \quad \dots(11.7)$$

Hence, we conclude from Eq. (11.4) that  $T_1 = T_2$ , i.e., in equilibrium the temperatures of the two phases must be the same.

$$(2) \quad \frac{\partial S}{\partial V} = K \frac{\partial \ln Z}{\partial V} = \frac{\langle p \rangle}{T} \quad \dots(11.8)$$

Therefore, relation (11.5) shows that the pressures of the phases must be the same.

$$(3) \text{ Since } \frac{\partial S}{\partial N} = -\frac{\mu}{T} \quad \dots(11.9)$$

The relation (11.6) leads to the condition

$$\mu_1(T, P) = \mu_2(T, P) \quad \dots(11.10)$$

## 11.2 CLASSIFICATION OF PHASE TRANSITIONS

Gibbs free energy is given by

$$G = \sum_i \mu_i N_i \quad [\text{see Eq. (6.80)}] \quad \dots(11.11)$$

Therefore, for processes which occur at constant pressure and temperature

$$dG = \sum_i \mu_i dN_i \quad \dots(11.12)$$

$$\text{Therefore } \mu_i = \frac{\partial G}{\partial N_i} \quad \dots(11.13)$$

Since at the phase transition  $\mu_1 = \mu_2$ , the derivatives of  $G$  with respect to  $N$  must be equal

$$\frac{\partial G}{\partial N_1} = \frac{\partial G}{\partial N_2} \quad \dots(11.14)$$

There is no restriction, however, on the derivatives of  $G$  with respect to  $P$  and  $T$ . The phase transitions are classified according to the behaviour of these derivatives.

If the derivatives  $\left(\frac{\partial G}{\partial P}\right)_{T,N}$  and  $\left(\frac{\partial G}{\partial T}\right)_{p,N}$  are discontinuous at the

transition point, that is  $V$  and  $S$  [refer to Eq. (6.80) or Eq. (11.28)] have different values in the two phases, the transition is called *first order transition*. If these derivatives are continuous, but higher derivatives are discontinuous at the transition point, the phase transition is said to be *continuous*. Typical behaviour of the Gibbs free energy and the entropy as a function of temperature at a transition point is shown in (Fig. 11.2).

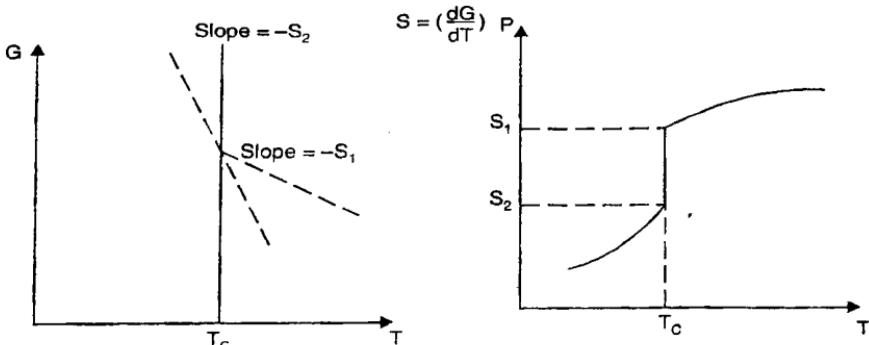


Fig. 11.2

### 11.3 PHASE DIAGRAM

The phases that are realized in nature for a given set of independent variables, are those with the lowest free energy. The Gibbs free energy is a function of  $T$ ,  $P$  and  $N$ . At constant temperature and pressure, Gibbs free energy is proportional to the number of particles, i.e.

$$G(T, P, N) = Ng(T, P) \quad \dots(11.15)$$

where  $g(T, P)$  is Gibbs free energy per particle and  $N$  is the number of particles. Since  $G$  is given by

$$G = \mu N \quad [\text{see Eq. (6.80)}]$$

$$\mu = g(T, P) \quad \dots(11.16)$$

Thus, chemical potential is the Gibbs free energy per particle. The equilibrium condition [Eq. (11.10)], therefore can be written as

$$g_1(T, P) = g_2(T, P) \quad \dots(11.17)$$

Hence, for equilibrium the Gibbs energy per particle in the two phases must be the same.

The relation (11.10) permits us to express one of the arguments of the chemical potential in terms of the other, provided we have the analytical expressions for the chemical potentials of both phases. Thus, we can express  $P$  as a function of  $T$ , i.e.

$$P = P(T) \quad \dots(11.18)$$

which defines a curve in the  $T$ - $P$  plane (Fig. 11.3)

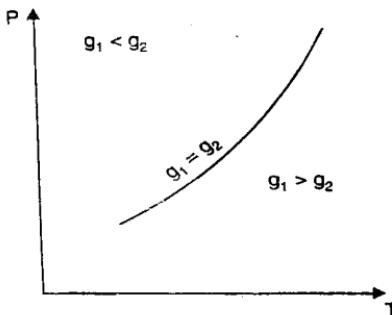


Fig. 11.3

At a point on the curve, the chemical potentials of the two phases are the same and it is only on this curve that the two phases can exist in equilibrium. It is known as a *phase equilibrium curve*. If the phases are liquid and vapour, it is called the *vapour pressure curve*; for solid and vapour it is the *sub-limitation curve* and for solid and liquid it is the *fusion curve*.

For a system consisting of a single component in two phases, the Gibbs free energy is given by

$$G = N_1 g_1 + N_2 g_2 \quad \dots(11.19)$$

where  $N_1, N_2$  are the number of particles in the two phases. We have shown above that for equilibrium  $g_1 = g_2$ . When this condition is satisfied, the relation (11.19) shows that the transfer of a particle from one phase to another does not change  $G$ .

A one-component system may also exist in three different phases, e.g. solid, liquid and vapour. The arguments similar to those presented above lead to the following equilibrium conditions:

$$g_1(T, P) = g_2(T, P) = g_3(T, P) \quad \dots(11.20)$$

We have seen that Eq. (11.17) defines a phase equilibrium curve. Equations (11.20) define three equilibrium curves.

$$g_1 = g_2; g_2 = g_3; g_1 = g_3$$

which meet at a point known as the *triple point* (Fig. 11.4).

The diagram in this figure is known as the *phase diagram*. The three phase equilibrium curves divided the  $T$ - $P$  plane into three regions in which solid, liquid and gaseous phases are in stable states, i.e. have the minimum Gibbs free energy. At the triple point ( $T_0, P_0$ ) all three phases are in equilibrium. For instance, for water the triple point occurs at

$$T_0 = 0.0078^\circ\text{C}, P_0 = 0.006 \text{ atmosphere} \quad \dots(11.21)$$

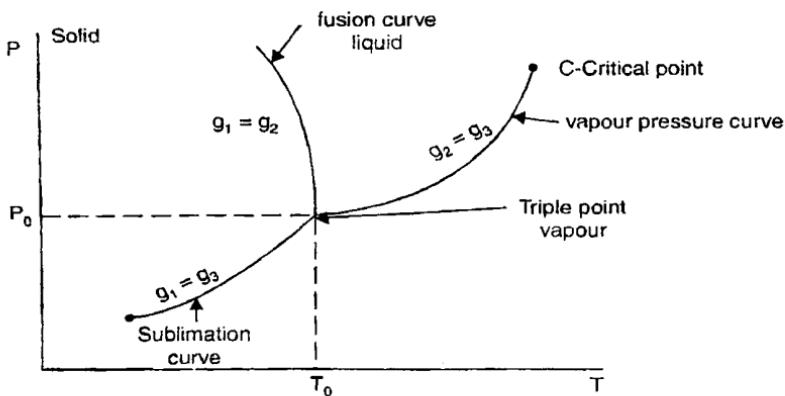


Fig. 11.4

It is clear from Fig. (11.4) that at a pressure lower than  $P_0$ , ice upon heating converts directly into vapour without going through the liquid phase, i.e. it sublimates.

The point at which the vapour pressure curve abruptly terminates (point *C*) is called the *critical point*. Above this point a substance can go continuously from a gaseous state to the liquid state without going through a phase transition.

## 11.4 CLAUSIUS-CLAPEYRON EQUATION

We have said above that the relation (11.10) permits us to express  $P$  in terms of  $T$ , which when plotted gives us the phase transition curve. We will now obtain the differential equation of this phase transition curve.

Taking derivatives of Eq. (11.10) we have the relation

$$\frac{\partial \mu_1}{\partial T} + \frac{\partial \mu_1}{\partial P} \frac{\partial P}{\partial T} = \frac{\partial \mu_2}{\partial T} + \frac{\partial \mu_2}{\partial P} \frac{\partial P}{\partial T}$$

Substituting these in Eq. (11.22), we have

$$-s_1 + V_1 \frac{\partial P}{\partial T} = -s_2 + V_2 \frac{\partial P}{\partial T}$$

where we used Eq. (6.78)

$$\text{i.e. } \frac{\partial P}{\partial T} = \frac{s_2 - s_1}{V_2 - V_1} \quad \dots(11.22)$$

Finally, since  $\delta q = T(S_2 - S_1)$ ,

$$\frac{\partial P}{\partial T} = \frac{\delta q}{T(V_2 - V_1)} \quad \dots(11.23)$$

This is known as the *Clausius-Clapeyron* equation. The derivative in this equation gives the rate of change of pressure along the equilibrium curve. It is clear from Eq. (11.23) that if  $\delta q > 0$ , the transition takes place with the absorption of heat, and further, if the transition is accompanied by an increase in volume, i.e.  $V_2 > V_1$  as in the case of boiling of water,

then  $\frac{dp}{dT} > 0$ , that is, the temperature rise with pressure. If, on the other hand,  $V_2 < V_1$  as in case of melting of ice, the phase transition temperature decreases with pressure. The slope  $\frac{dp}{dT}$ , therefore, is positive or negative depending on the nature of the substance. Water is an example of a system whose fusion curve has a negative slope.

In order to obtain the dependence of  $P$  on  $T$ , i.e.  $P = P(T)$ , we have to integrate Eq. (11.23). For this, we have to express  $V_1$  and  $V_2$  as functions of  $P$  and  $T$ , which is possible if we know the equation of state for the two phases. We show below how this dependence is obtained in some particular cases and illustrate its use in finding expressions for some thermodynamic quantities.

### 1. Liquid-Vapour equilibria:

(a) **Vapour pressure curve:** In this case, at temperatures lower than the critical point  $V_2 \gg V_1$ , the vapour is so rarefied that we may neglect the change in volume in the liquid and assume that the vapour obeys the ideal gas laws, i.e.  $PV = RT$

$$\text{Therefore} \quad \frac{dP}{dT} = \frac{P\delta q}{RT^2} \quad \dots(11.24)$$

Integrating, we have

$$P = P_0 e^{-\delta q/RT} \quad \dots(11.25)$$

This shows that as the temperature is increased, the vapour pressure increases, and  $\delta q$  is a latent heat of vaporization.

(b) **Heat capacity of vapour in equilibrium:** The Clausius-Clapeyron equation can be used to solve a number of problems, while we are at the liquid-vapour equilibrium. Let us see how the heat capacity of a vapour in equilibrium with its liquid phase can be obtained using Eq. (11.23).

Since entropy is a function of pressure and temperature, heat capacity

$$\begin{aligned} C_{\text{equi}} &= \left(\frac{\partial Q}{\partial T}\right)_{\text{equi}} = T\left(\frac{\partial S}{\partial T}\right)_{\text{equi}} \\ &= T\left(\frac{\partial S}{\partial T}\right)_p + T\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial p}{\partial T}\right)_{\text{equi}} \end{aligned} \quad \dots(11.26)$$

We know that

$$T\left(\frac{\partial S}{\partial T}\right)_p = C_p$$

$$\text{Now } dE = TdS - pdV = d(TS) - SdT - d(pV) + Vdp$$

$$\text{or } d(E - TS + pV) = -SdT + Vdp \quad \dots(11.27)$$

$$\text{i.e. } dG = -SdT + Vdp \quad [\text{see Eq. (6.80)}]$$

$$\text{Therefore } \left(\frac{\partial G}{\partial T}\right)_p = -S; \left(\frac{\partial G}{\partial p}\right)_T = V \quad \dots(11.28)$$

Equality of cross derivatives implies

$$\begin{aligned} \frac{\partial^2 G}{\partial p \partial T} &= \frac{\partial^2 G}{\partial T \partial P} \\ -\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_p \end{aligned} \quad \dots(11.29)$$

Substituting in Eq. (11.26)

$$C_{\text{equi}} = C_p - T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P}{\partial T}\right)_{\text{equi}} \quad \dots(11.30)$$

Assuming that the vapour behaves like an ideal gas, the equation of state is

$$PV = RT$$

$$\frac{\partial V}{\partial T} = \frac{R}{P}$$

Hence

$$C_{\text{equi}} = C_p - T \frac{R}{p} \frac{p\delta q}{RT^2} = C_p - \frac{\delta q}{T} \quad \dots(11.31)$$

**(c) Compressibility of vapour:** Compressibility of vapour

$\frac{1}{V^2} \left( \frac{dV_2}{dP_2} \right)$  along the equilibrium phase curve can be found as follows:

$$\begin{aligned} \left( \frac{dV_2}{dP} \right) &= \left( \frac{\partial V_2}{\partial P} \right)_T + \left( \frac{\partial V_2}{\partial T} \right)_p \left( \frac{\partial T}{\partial P} \right) \\ &= \left( \frac{\partial V_2}{\partial P} \right)_T + \left( \frac{\partial V_2}{\partial T} \right)_p \frac{T(V_2 - V_1)}{\delta q} \end{aligned} \quad \dots(11.32)$$

At  $T \ll T_c$ , we can assume  $V_2 = \frac{RT}{P}$

$$\text{Therefore } \frac{dV_2}{dP} = -\frac{RT}{P^2} + \frac{R}{P} \cdot \frac{T \cdot RT}{P \delta q} = -\frac{RT}{P^2} \left( 1 - \frac{RT}{\delta q} \right) \quad \dots(11.33)$$

The compressibility is

$$\begin{aligned} \frac{1}{V^2} \left( \frac{dV_2}{dP} \right) &= -\frac{P}{RT} \frac{RT}{P^2} \left( 1 - \frac{RT}{\delta q} \right) \\ &= -\frac{1}{P} \left( 1 - \frac{RT}{\delta q} \right) \end{aligned} \quad \dots(11.34)$$

**2. Sublimation curve:** We can obtain a fairly simple equation for the sublimation curve.

The enthalpy  $H$  is given by

$$H = E + PV$$

$$\begin{aligned} \text{Therefore } dH &= dE + PdV + VdP = TdS + VdP \\ &= C_p dT + VdP \end{aligned} \quad \dots(11.35)$$

Since the vapour pressure along the sublimation curve is generally small, we can neglect the variation in pressure and write.

$$dH = C_p dT \quad \dots(11.36)$$

Therefore, the molar enthalpy of the solid at a point on the curve is

$$H_s = H_s^0 + \int_0^T C_p^s dT \quad \dots(11.37)$$

and that of the vapour is

$$H_v = H_v^0 + \int_0^T C_p^v dT \quad \dots(11.38)$$

where  $H_s$ ,  $H_v$  are the molar enthalpies of the solid and vapour at zero pressure and temperature.

Using these values for the enthalpy we can write the Clausius-Clapeyron equation as

$$\frac{dP}{dT} = \frac{P \Delta H_{vs}}{RT^2} \quad \dots(11.39)$$

where

$$\Delta H_{vs} = H_v - H_s \text{ and } V_2 - V_1 = \frac{RT}{P}$$

or

$$\frac{dP}{dT} = \frac{P}{RT^2} \left[ \Delta H_{vs}^0 + \int_0^T C_p^V dT - \int_0^T C_p^s dT \right]$$

Noting that for a monatomic vapour  $C_p = \frac{3}{2}R$  and integrating the above equation,

we have

$$\ln P = -\frac{\Delta H_{vs}^0}{RT} + \frac{3}{2} \ln T - \frac{1}{R} \int_0^T \frac{T C_p^s dT}{T^2} dT + \text{constant} \quad \dots(11.40)$$

Here  $\Delta H_{vs}^0$  is the *latent heat of sublimation*.

## 11.5 VAN DER WAAL'S EQUATION

We have derived van der Waal's equation in Sec. 6.13. This equation, though not the most accurate, is the simplest equation of state, which exhibits many essential features of the liquid-vapour phase transition. The equation is

$$\left( P + \frac{a}{V^2} \right) (V - b) = RT \quad \dots(11.41)$$

On transformation it takes the form

$$v^3 = \left( b + \frac{RT}{P} \right) v^2 + \frac{a}{P} V - \frac{ab}{P} = 0 \quad \dots(11.42)$$

A third degree equation with real coefficients can have either one real and two complex roots or three real roots. Therefore, an isotherm plotted on a  $P$ - $V$  plane using Eq. (11.42) will be crossed by a straight line parallel to the  $V$ -axis, either at three points or at one.

The general form of the curves representing Eq. (11.42) is shown in Fig. 11.5. For each curve  $T$  remains constant. Higher curves correspond to higher values of  $T$ . With rising temperature, the portion of van der Waal's isotherms on which humps and valleys are observed diminishes and at a certain temperature — *critical temperature*,  $T_c$ , it turns into a point of inflexion.

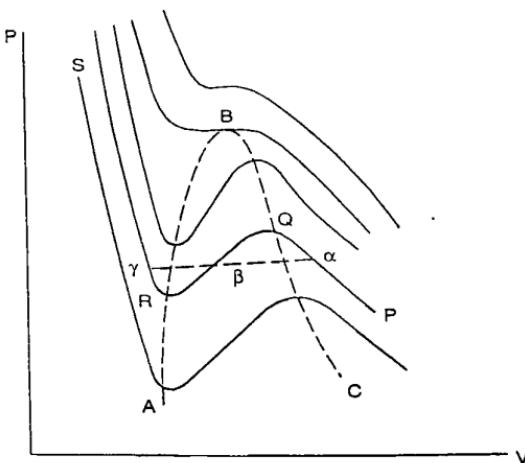


Fig. 11.5

Let us now commence searching for maxima and minima. We can write van der Waal's equation in the form

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \dots(11.43)$$

We differentiate this equation to obtain  $\frac{\partial P}{\partial V}$  and equate it to zero for finding the turning point of the curve.

$$\text{Therefore } \frac{\partial P}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \quad \dots(11.44)$$

Eliminating  $T$  between this equation and Eq. (11.43)

$$P = \frac{a(V-2b)}{V^2} \quad \dots(11.45)$$

This equation gives the locus of the maxima and minima of the family of curves obtained for different values of  $T$  and is represented by the dotted line ARBQC. This curve divides the  $P$ - $V$  plane into three regions. The region bounded by the curve  $AB$  and the upper point of the critical isotherm represents the liquid state region. The region located inside the dome-shaped curve  $ABC$  describes two phase states, liquid and vapour. To the right of the curve  $BC$ , it is the vapour state region. The curve  $ABC$  is the *co-existence curve*. To find the maximum  $B$  of this curve, we differentiate Eq. (11.45) with respect to  $V$  and equate it to zero. We get

$$V_c = 3b \quad \dots(11.46)$$

$$\text{Therefore } P_c = \frac{a}{27b^2}$$

Substituting these in Eq. (11.43), we have

$$T_c = \frac{8a}{27Rb} \quad \dots(11.47)$$

These are the values of  $P$ ,  $V$ ,  $T$ , at the critical point. Actually, the curve corresponding to the critical temperature has a point of inflexion. At pressures higher than  $P_c$  and temperature above  $T_c$ , no difference of phase exists. At the critical point the two phases become identical.

Away from the critical point van der Waal's equation provides a remarkably good fit to experiment. Close to the critical point, however, the theory breaks down and does not provide an adequate fit to modern experimental data.

An interesting feature of the van der Waal's equation is that, it can be expressed, as shown below, in a universal form.

Let us replace the pressure, volume and temperature in the van der Waal's equation by dimensionless parameters.

$$\text{(reduced pressure)} \quad \bar{P} = \frac{P}{P_c}; \text{(reduced volume)} \quad \bar{V} = \frac{V}{V_c}$$

$$\text{and (reduced temperature)} \quad \bar{T} = \frac{T}{T_c}.$$

The transformed equation becomes

$$\left( \bar{P} + \frac{3}{\bar{V}^2} \right) (3\bar{V} - 1) = 8\bar{T} \quad \dots(11.48)$$

We see that in this equation all individual parameters, constants  $a$  and  $b$  are eliminated. Most substances when plotted in terms of reduced parameters lie approximately in the same curve and, thus satisfy the *law of corresponding states*, which states that all fluids when described in terms of reduced parameters, obey the same equation of state. The general agreement between the van der Waal equation and experiment is remarkable. However, the law of corresponding states is in a far more exact agreement with experimental results than the van der Waal equation.

We have seen that van der Waal's equation predicts an S-shaped curve like  $PQRS$ . Experiments, however, show that under ordinary conditions, a real phase transition does not follow this curve, but is represented by  $PQRS$  curve.

This is the actual physical isotherm and is in accordance with our expectations, since pressure does not undergo a discontinuous jump in a phase transition. The portion  $QR$  represents essentially an unrealizable situation, in which increase in pressure causes increase in volume, thus

violating the stability condition  $\frac{\partial P}{\partial V} \leq 0$ .

However, since  $\frac{\partial P}{\partial V}$  is negative on the segments  $\alpha Q$  and  $\gamma R$ , their existence cannot be ruled out. Under certain conditions it is possible to realize experimentally the portion  $\gamma R$  which correspond to a *supercooled vapour* and *superheated liquid*, respectively. These states are not absolutely stable. Under a small external perturbation, the system rapidly goes to the nearest stable state. Such states are called *metastable states*. Van der Waal's theory gives no indication of the point at which condensation of the liquid state begins. The position of the line  $\alpha \beta A$  can be determined by a consideration of the change in the appropriate thermodynamical function of state.

We know that the work done in an isothermal process is equal to the decrease in the free energy. For the work done along the isotherm  $PQRS$ , we have

$$dW = \int_{PQRS}^P PdV = F_R - F_Q \quad \dots(11.49)$$

The free energy is given by

$$F = \mu N - pV \quad [\text{see Eq. (6.79)}]$$

At equilibrium the chemical potentials of the phases are equal.

$$\begin{aligned} \text{Therefore } F_R + PV_R &= F_Q + PV_Q \\ \text{i.e. } F_R - F_Q &= P(V_Q - V_R) \end{aligned} \quad \dots(11.50)$$

$$\text{or } \int_{PQRS}^P PdV = P(V_Q - V_R) \quad \dots(11.51)$$

This shows that the integral along the van der Waal's curve is equal to the area of the rectangle below the isobar  $RS$  and consequently

$$\text{area I} = \text{area II} \quad \dots(11.52)$$

When this condition is satisfied  $P \propto \gamma S$  gives the equilibrium state of the system. The method of realizing the condition (11.52) is called Maxwell's construction. Thus, we observe on the  $P$ - $V$  diagram a discontinuity jump in volume,  $V_2 - V_1$  the magnitude of which is determined by Maxwell's equal area rule.

## 11.6 SECOND-ORDER PHASE TRANSITIONS

We have discussed so far the first-order phase transitions in which the chemical potential changes continuously at the transition point (at

which  $\mu_1 = \mu_2$ ) and their first derivatives  $\left(\frac{\partial \mu}{\partial T}\right)_p = -S$  and  $\left(\frac{\partial \mu}{\partial P}\right)_T = V$

undergo discontinuity jumps. As stated in Sec. 11.2 there also exist continuous transitions in which these first derivatives do not undergo any discontinuous jumps — i.e. at the transition point  $S_1 = S_2$  and  $V_1 = V_2$  —

but its higher derivatives may have finite or infinite discontinuities. In this section we confine our discussion to the so-called *second-order phase transitions*, during which the second derivatives of the chemical potential undergo discontinuous jumps at the transition point. Thus, second-order phase transitions do not involve discontinuity jumps in volume and in

entropy, but involve abrupt changes in heat capacity  $\left\{ \left( \frac{\partial^2 \mu}{\partial T^2} \right)_p = -\frac{C_p}{T} \right\}$

and compressibility  $\left\{ \left( \frac{\partial^2 \mu}{\partial p^2} \right)_T = \left( \frac{\partial V}{\partial p} \right)_T \right\}.$

Second-order phase transitions are usually associated with the abrupt changes in various properties characterizing the symmetry of a body. For example, when a magnetic material changes its state from a ferromagnetic material to a paramagnetic material, the symmetrical arrangement of the elementary magnetic moments undergoes a discontinuity jump and the symmetry changes. Such transitions which involve a broken symmetry and a continuous change in the slope of the free energy curve can be described by a theory due to Ginzburg and Landau.

## 11.7 GINZBURG-LANDAU (GL) THEORY

The basic idea of this theory is that, a phase transition can be considered as going from an ordered to a disordered phase. Consider for example, a three-dimensional magnetic system consisting of an array of dipoles. If the interaction between the dipoles is ferromagnetic, then in the ground state at  $T = 0$ , all the dipoles will be aligned. In this state the internal energy  $U$  is minimum and the entropy  $S$  is zero. For  $T > 0$ , some dipoles go out of alignment because of thermal agitation, but in such a way as to increase both  $S$  and  $U$  and minimize the free energy  $F = U - TS$ .

The GL theory assumes that a physical system can be characterized, in addition to the ordinary physical parameters  $P$ ,  $T$ , etc., also by a macroscopic parameter called the *order parameter*, which appears in a less symmetric phase. The order parameter may be a scalar, a vector, a tensor or some other quantity. In the first-order transitions, there is a discontinuous jump in the state of the system, because its volume and entropy change abruptly — and hence, there need not be any relationship between the symmetry properties of the two phases. But for a continuous transition, the state changes continuously and the symmetry properties of the two phases are closely related.

The thermodynamic potential of the system, therefore, is of the type  $G(P, T, \eta)$ . The variable  $\eta$  which represents the order parameter, is slightly on a different footing from  $P$  and  $T$ . While the latter can be given arbitrary values,  $\eta$  will be determined by the condition that  $G$  is minimum.

Suppose for simplicity, that the order parameter is a vector  $\eta$  associated with the less symmetric phase. The free energy must be such that it will be minimized for  $\eta = 0$  above the transition and for  $\eta \neq 0$  below the transition.

Further, the free energy must be a scalar function of the order parameter. Hence, if the order parameter is a vector, as we have assumed, the free energy can only depend on the scalar products of the order parameter.

In general, we can expand the free energy  $G(T, \eta)$  near the transition point, in the form

$$G(T, \eta) = G_0(T) + \alpha_2(T) \eta^2 + \alpha_4(T) \eta^4 + \dots \quad \dots(11.53)$$

Note that, the first-order and third-order terms are not included, because we cannot construct a scalar from them.

We have now to choose the forms of  $\alpha_2$  and  $\alpha_4$ .

We see from Eq. (11.53) that the free energy is minimum at the critical temperature  $T_c$  and above it if  $|\eta| = 0$ . For  $T < T_c$  we have to choose  $\alpha_2$  in such a way that the free energy is minimum for  $|\eta| \neq 0$ . Further, at the transition temperature  $T = T_c$ ,  $\alpha_2(T_c)$  must be zero, since the energy varies continuously through the transition point. All these conditions are satisfied if we put  $\alpha_2(T)$  in the form

$$\alpha_2(T) = \alpha_0 (T - T_c) \quad \dots(11.54)$$

where  $\alpha_0$  is a function of  $T$ .

Since the energy must increase if  $|\eta|$  is increased to a very high value, we have to assume  $\alpha_4(T)$  to be positive

$$\alpha_4(T) > 0 \quad \dots(11.55)$$

For the free energy to be minimum, we must have

$$(i) \frac{\partial G}{\partial \eta} = 0; (ii) \frac{\partial^2 G}{\partial \eta^2} > 0 \quad \dots(11.56)$$

The first of these conditions gives

$$\frac{\partial G}{\partial \eta} = 2\alpha_2 \eta + 4\alpha_4 \eta |\eta|^2 = 0 \quad \dots(11.57)$$

Therefore either  $\eta = 0$  or  $\eta = \pm \sqrt{\frac{-\alpha_2}{2\alpha_4}} \hat{n}$

$$= \pm \sqrt{\frac{-\alpha_0(T - T_c)}{2\alpha_4}} \hat{n} \quad \dots(11.58)$$

Thus, when  $\alpha_2 > 0$ , the minimum occurs for  $\eta = 0$  and when  $\alpha_2 < 0$ ,

the minimum occurs for  $\eta = \pm \sqrt{\frac{-\alpha_2}{2\alpha_4}} \hat{n}$ . The variation of free energy for the two cases is shown in Fig. 11.6.

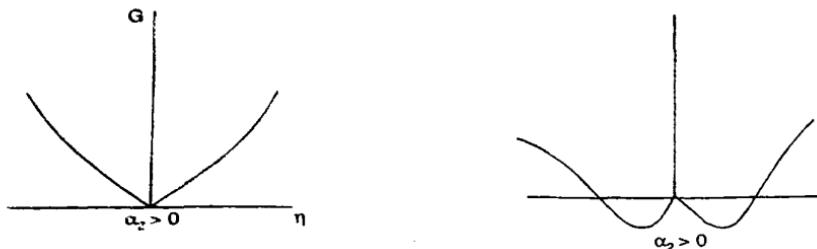


Fig. 11.6

The free energy above the transition point is given by

$$G(T, \eta) = G_0(T) \text{ for } T > T_c \quad \dots(11.58A)$$

and below it by

$$\begin{aligned} G(T, \eta) &= G_0(T) + \alpha_2(T)\eta^2 + \alpha_4(T)\eta^4 \\ &= G_0(T) - \frac{\alpha_0^2(T - T_c)^2}{2\alpha_4} + \alpha_4(T) - \frac{\alpha_0^2(T - T_c)^2}{4\alpha_4^2} \\ &= G_0(T) - \frac{\alpha_0^2(T - T_c)^2}{4\alpha_4} \text{ for } T < T_c \quad \dots(11.59) \end{aligned}$$

We may recall that  $C_p$  is given by

$$C_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right) \quad \dots(11.60)$$

$$\text{Hence } C_p(T < T_c)_{T=T_c} = T_c \frac{\alpha_0^2}{2\alpha_4} \quad \dots(11.61)$$

$$\text{and } C_p(T > T_c)_{T=T_c} = 0$$

Therefore the jump in the heat capacity is

$$C_p(T < T_c)_{T=T_c} - C_p(T > T_c)_{T=T_c} = T_c \frac{\alpha_0^2}{2\alpha_4} \quad \dots(11.62)$$

Figure 11.7 shows the specific heat as a function of temperature. The curve shows the discontinuity in the specific heat at  $T_c$ .

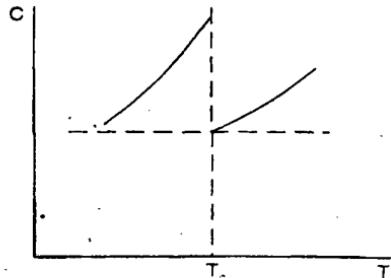


Fig. 11.7

## 11.8 PHASE TRANSITION IN FERROMAGNETIC MATERIALS

For magnetic transitions we have a situation similar to that of gas—liquid transition. Figure 11.8 shows the isotherms drawn for different temperatures. If an external magnetic field  $H$  is applied to a system, magnetization  $M$  is included in it in a direction depending upon the direction of the field. For temperatures below the critical temperature  $T < T_c$ , residual or spontaneous magnetization  $M_0$  remains in the system when the field  $H$  is switched off; whereas for  $T > T_c$  there is no residual magnetization.

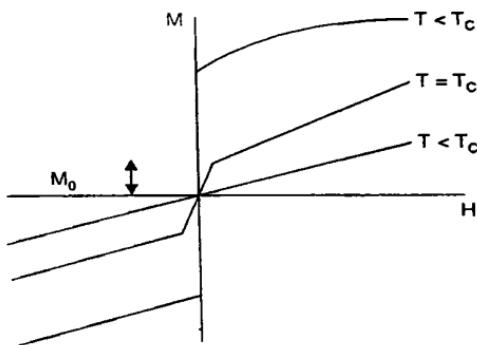


Fig. 11.8

There is a close analogy between gas and magnetic system, which can be seen if one compares Figs. 11.5 and 11.8 and identifies  $M$  with  $V$  and  $H$  with  $P$ . The striking difference between the two systems is that, in the magnetic case the flat parts of the isotherms are on top of one another.

A simple example of a transition is the transition from a paramagnetic to a ferromagnetic system. The magnetic moments in a paramagnetic substance above the Curie temperature are randomly oriented and there is no yet magnetization. The paramagnetic system at this temperature is rotationally invariant. As the temperature is lowered, magnetic interaction energy becomes more important than the thermal energy, magnetic moments become ordered and this gives rise to magnetization. The symmetry that is broken in this transition is rotation symmetry.

If  $M$  is the average magnetization of the system, Helmholtz free energy can be expressed as

$$F(M, T) = F(0, T) + \alpha_2(T)M^2 + \alpha_4(T)M^4 \quad \dots(11.62A)$$

If an external magnetic field  $H$  is applied to the system, Gibbs free energy of the system can be expressed as

$$\begin{aligned} G(H, T) &= F(M, T) - H \cdot M \\ &= F(0, T) - H \cdot M + \alpha_2(T)M^2 + \alpha_4(T)M^4 \end{aligned} \quad \dots(11.63)$$

This is minimized when

$$\left( \frac{\partial G}{\partial M} \right)_T = -H + 2\alpha_2(T)M = 0 \quad \dots(11.64)$$

where we have considered only the lowest order in  $M$ .

Therefore  $M = \frac{1}{2\alpha_2}H$  ...(11.65)

This shows that above the Currie-point, non-zero magnetization is possible.

Below the Currie-point, the isothermal susceptibility is given by

$$\chi = \left( \frac{\partial M}{\partial H} \right)_T = \frac{1}{2\alpha_2} = \frac{1}{2\alpha_0(T - T_c)} \quad \dots(11.66)$$

It is obvious from this relation that at  $T = T_c$ , the susceptibility becomes infinite. Therefore, at the critical point even a small external field may have a large effect on magnetization.

Below the critical point, as shown in the preceding section

$$M = \sqrt{\frac{\alpha_0(T_c - T)}{2\alpha_4}} \quad \dots(11.67)$$

Therefore  $\frac{\partial M}{\partial T} = -\frac{1}{2} \sqrt{\frac{\alpha_0(T_c - T)}{2\alpha_4}}$  ...(11.68)

Clearly, the magnetization increases abruptly below the critical point.

Let us now calculate the chemical potential, the entropy and the volume of the magnetic material

(i) From Eq. (11.63) when  $H = 0$

$$\mu = G(M, T) = F(0, T) + \alpha_2(T)M^2 + \alpha_4(T)M^4 \quad \dots(11.69)$$

In the paramagnetic domain ( $M = 0$ )

$$\mu_p = F(0, T) \quad \dots(11.70)$$

and in the ferromagnetic domain

$$\mu_f = F(0, T) - \frac{\alpha_2^2}{4\alpha_4} \quad \dots(11.71)$$

(ii) Entropy in the paramagnetic domain

$$S_p = -\frac{\partial F}{\partial T} \quad \dots(11.72)$$

while in ferromagnetic domain it is

$$S_f = -\frac{\partial F}{\partial T} + \frac{\alpha_2 \{ 2\alpha_4 \alpha_{2I}^1 - \alpha_2 \alpha_{4I}^1 \}}{4\alpha_4^2} \quad \dots(11.73)$$

At the critical temperature  $\alpha_2 = 0$

Therefore  $S_p = S_f$

$$(iii) \text{ Volume} \quad V_p = \frac{\partial \mu}{\partial p} = \frac{\partial F}{\partial p} \quad \dots(11.74)$$

and

$$V_F = \frac{\partial F}{\partial p} - \frac{\alpha_2 \{2\alpha_4\alpha'_{2p} - \alpha_2\alpha'_{4p}\}}{4\alpha_4^2} \quad \dots(11.75)$$

(because  $\alpha_2 = 0$  at  $T = T_c$ ;  $V_F = \frac{\partial F}{\partial p}$ )

Hence  $V_p = V_F \quad \dots(11.76)$

Thus, there is no discontinuity jump in entropy and volume at the Currie point.

Let us now investigate whether there is any discontinuity jump in the heat capacity at the Currie point

$$\begin{aligned} C_p &= T_c \frac{\partial(S_f - S_p)}{\partial T} = T_c \frac{\partial}{\partial T} \frac{\{2\alpha_4\alpha'_2 - \alpha_2\alpha'_{4T}\}}{4\alpha_4^4} \\ &= T_c \frac{\alpha'^2_{2T}}{2\alpha_4} \quad \dots(11.77) \end{aligned}$$

(because  $\alpha_2 = 0$  at  $T = T_c$ )

Since  $\alpha_4 > 0$  heat capacity in the ferromagnetic state is larger than that in the paramagnetic state.

In the same way we can show that the compressibility in the ferromagnetic state exceeds that in the paramagnetic state.

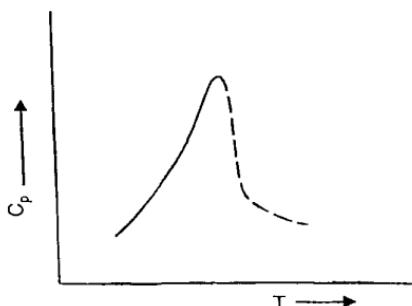


Fig. 11.9

### 11.9 LIQUID HELIUM

Helium has proven to be one of the most remarkable elements in nature, particularly from the standpoint of statistical physics. It is the only substance which remains liquid under ordinary pressure at absolute zero; all others freeze to the solid state if sufficiently cooled. Solidification of helium takes place under external pressure exceeding 25 atmospheres.

According to classical concepts, at absolute zero, all the atoms of a substance cease to move and occupy fixed positions with the body, thus causing it to become a solid. The fact that helium remains a liquid at this temperature, indicates that entirely different concepts of quantum mechanics are required for its understanding.

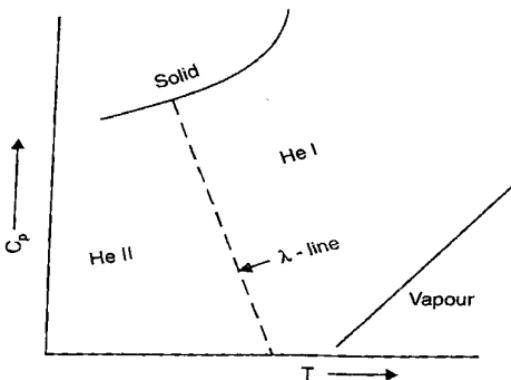


Fig. 11.10

Helium atoms occur in nature in two stable isotopic forms,  $^3\text{He}$  and  $^4\text{He}$ . The former is rarer of these two isotopes. Chemically both these are virtually identical. The only difference between them is a difference of mass and that  $^3\text{He}$  has a nuclear spin  $\frac{1}{2}$  while  $^4\text{He}$  has spin zero.  $^3\text{He}$ , therefore, obeys Fermi-Dirac statistics, while  $^4\text{He}$  obeys Bose-Einstein statistics.

Because of the difference in their statistics, the two systems exhibit very different behaviour upon cooling.  $^4\text{He}$ , which is a boson liquid, exhibits a second-order transition to a superfluid state. This was first observed as an abrupt jump in the liquid's specific heat (Fig. 11.9).  $^3\text{He}$  also undergoes a transition to a superfluid state, but at a much lower temperature  $\sim 2.7 \times 10^{-3}\text{K}$ . The mechanisms of the two transitions, however, are different. The co-existence curves for liquid  $^4\text{He}$  are shown in Fig. 11.10. At a low temperature,  $^4\text{He}$  has four phases: a solid phase, two liquid phases and a vapour phase. As the normal liquid is cooled, a line of  $\lambda$ -point occurs near  $2\text{ K}$ , the exact value of temperature depends upon pressure. The  $\lambda$ -point line indicates that a continuous phase transition has occurred. Liquid helium above the  $\lambda$ -line is called Helium I (He I) and that below it He II. It is the latter that shows unique properties. Initial experiments with liquid helium  $^4\text{He}$  showed that it was able to leak out of its container through cracks so tiny that even  $^4\text{He}$  gas could not leak through. Apparently it has no viscosity.

Further light on the properties of helium is thrown by a remarkable experiment first performed by Andronikashvili.

A very closely spaced pile of disks is suspended on a fibre (Fig. 11.11). The set of disks can perform rotational oscillations about the fibre as the axis. The period of oscillations depends on the mass of the disks and, hence, mass of the disks can be determined from the period of oscillations. The disks are immersed in He I and the period of oscillations measured. It was found that the helium trapped between the disks is carried around with them and effectively adds to their mass. If the temperature is lowered below  $\lambda$ -point, it is found that the mass of helium carried with the disk rapidly diminishes and around 1 K virtually none moves with the disk.

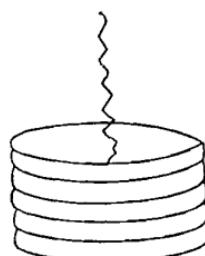


Fig. 11.11

These properties of He II, are described well by a two-fluid model. It is assumed that He II is a mixture of the two fluids: the normal fluid and the superfluid and that there is no viscous interaction between them. While the normal fluid has all the usual properties of a fluid, superfluid has some curious properties. It has zero entropy and no viscosity.

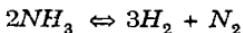
### 11.10 CHEMICAL EQUILIBRIUM

Chemical reactions are usually written in the form



or more generally  $\sum_i v_i A_i = 0 \quad \dots(11.79)$

where  $A_i$  are the chemical symbols for reacting substances and  $v_i$  are integers (+ve or -ve) giving the number of molecules of each substance. Consider, for example, the reaction



This can be written as



Here  $v_{H_2} = 3$ ;  $v_{N_2} = 1$ ; and  $v_{NH_3} = -2$

Along with the direct chemical reaction, reverse reaction also can take place. However, such reactions ultimately lead to an equilibrium state in which the two opposite reactions occur at rates such that the number of particles of each reacting substance remains constant. This equilibrium is called the *chemical equilibrium*.

### 11.11 CONDITION FOR CHEMICAL EQUILIBRIUM

In equilibrium Gibbs free energy must have its lowest possible value. That is

$$dG = -SdT + VdP + \sum_i \mu_i v_i = 0 \quad \dots(11.80)$$

Let us assume that the reaction occurs at constant pressure and temperature. Under these conditions Eq. (11.80) reduces to

$$\sum_i \mu_i v_i = 0 \quad \dots(11.81)$$

This is condition for chemical equilibrium.

## 11.12 THE LAW OF MASS ACTION

Let us now apply the condition of equilibrium Eq. (11.81) to a reaction taking place in a mixture of ideal gases.

The chemical potential for the translational modes of each gas as given by Eq. (6.94) is

$$\begin{aligned} \mu_i &= -kT \ln \left\{ \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} \frac{1}{N_i} \right\} \\ &= -kT \ln \left\{ \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} \frac{kT}{p_i} \right\} \end{aligned} \quad \dots(11.82)$$

where  $p_i$  is the partial pressure of the  $i$ th gas. In addition to the translational mode, there are rotational, vibrational and electronic modes of excitation possible in a molecule. We, therefore, introduce a factor  $Z_i$  in the above expression for  $\mu_i$  which represents the contribution from these internal modes to the partition function.

Thus

$$\mu_i = -kT \ln \left\{ \left( \frac{2\pi m_i kT}{h^2} \right)^{3/2} Z_i \frac{kT}{p_i} \right\} \quad \dots(11.83)$$

Substitution this in Eq. (11.81), we have

$$\sum \left[ -v_i kT \ln \left\{ \left( \frac{2\pi}{h^2} \right)^{3/2} m_i^{3/2} Z_i (kT)^{5/2} \right\} + v_i kT \ln p_i \right] = 0$$

i.e.

$$\sum \ln p_i^{v_i} = \sum \ln \left\{ \left( \frac{2\pi}{h^2} \right)^{3/2} m_i^{3/2} Z_i (kT)^{5/2} \right\}^{v_i}$$

or

$$\begin{aligned} \prod P_i^{v_i} &= \left\{ \left( \frac{2\pi}{h^2} \right)^{3/2} (kT)^{5/2} \right\}^{\sum v_i} \prod m_i^{v_i} \prod Z_i^{v_i} \\ &= K(P, T) \end{aligned} \quad \dots(11.84)$$

This is called the *law of mass action*. The quantity  $K(P, T)$  is called the *chemical equilibrium constant* and is a function of pressure and temperature.

Since  $v_i$  may have +ve as well as -ve values, the right-hand side of Eq. (11.84) [viz.  $K(P, T)$ ] is actually a fraction with a numerator representing the partial pressures of appearing substances and denominator representing the partial pressures of disappearing substances. One can easily see from Eq. (11.84) that greater the reaction constant  $K(P, T)$ , greater is the shift of the equilibrium in the direction of end products.

It must be mentioned here that the partition function appearing in the formula (11.84) needs a correction. It is conventional to measure the energies of the molecules from the ground state and use the partition function  $Z_r = \sum e^{-\beta \epsilon_r}$ . However, a certain amount of energy is required to form a molecule of a certain species  $r$  in its ground state from the constituted atoms in their ground states. If this energy is represented by  $\epsilon_r^*$  the correct partition function will be

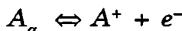
$$Z = \sum e^{-\beta(\epsilon_r + \epsilon_r^*)} = e^{-\beta \epsilon_r^*} \sum e^{-\beta \epsilon_r} = Z_r e^{-\beta \epsilon_r^*} \quad \dots(11.85)$$

We shall now consider a couple of examples to illustrate the application of the law of mass action.

### 11.13 SAHA IONIZATION FORMULA

At a very high temperature, collisions between gas particles may lead to the ionization of atoms. We shall consider in this section *thermal ionization* of a monatomic gas.

Ionization equilibrium can be considered as a particular case of chemical equilibrium. The equation of reaction is



$$\text{i.e. } A^+ + e^- - A_a = 0 \quad \dots(11.86)$$

where  $A_a$  denotes the neutral atom,  $A^+$  the singly ionized atom and  $e^-$  the electron. The stoichiometric coefficients of the reaction are

$$v_+ = 1, v_- = 1, v_a = -1$$

The equilibrium constant  $K(P, T)$  in this case is

$$K(P, T) = \frac{P_i P_e}{P_a} = \left( \frac{2\pi}{h^2} \right)^{3/2} (kT)^{5/2} \left( \frac{m_i m_e}{m_a} \right)^{3/2} \frac{Z_i Z_e}{Z_a} e^{-\epsilon^*/kT} \quad \dots(11.87)$$

where  $\epsilon^*$  is the ionization energy of the atom. For atoms and ions the only internal states are the electronic states and, hence, we may replace the partition function  $Z_i, Z_e, Z_a$  by the ground state degeneracies  $g_i, g_e, g_a$ . Further for electrons  $g_e = 2$ . Therefore, Eq. (11.87) can be written as

$$K(P, T) = \frac{P_i P_e}{P_a} = \left( \frac{2\pi}{h^2} \right)^{3/2} (kT)^{5/2} m_e^{3/2} \frac{2g_i}{g_a} e^{-\epsilon^*/kT} \quad \dots(11.88)$$

(because  $m_i \approx m_a$ )

This problem was first considered by Saha and Eq. (11.88) is due to him. It is used in problems with regard to astrophysics, electrical conductivity in flames, formation of ionosphere, determination of electron affinity in halogens, etc.

Equation (11.88) can be expressed in terms of fraction  $\alpha$  in the total number of particles.

$$\alpha = \frac{P_e}{P}, \text{ where } P = P_a + P_i + P_e$$

In neutral plasma the number of ions equals the number of electrons, i.e.  $P_i = P_e$ .

Therefore

$$\frac{P_i P_e}{P_a} = \frac{P(P_e / P)^2}{1 - 2\left(\frac{P_e}{P}\right)} = \frac{P\alpha^2}{1 - 2\alpha}$$

Hence

$$\frac{\alpha^2}{1 - 2\alpha} = \left(\frac{2\pi m_e}{h^2}\right)^{3/2} \frac{(kT)^{5/2}}{P} \frac{2g_i}{g_a} e^{-\epsilon^*/kT}$$

...(11.89)

## 11.14 DISSOCIATION OF MOLECULES

Molecules which are stable at a low temperature often dissociate at a high temperature. Let us consider a reaction of the type:



Suppose, the temperature is such that the molecules are not ionized but their rotational modes are fully excited. We can, therefore, replace the electron partition functions by  $g_m$  and  $g_a$ , the ground state degeneracies of the molecules and atoms, respectively. Equation (11.86) then becomes

$$K(P, T) = \frac{P_{0i}^2}{P_m} = \left(\frac{2\pi}{h^2}\right)^{3/2} (pT)^{5/2} \left(\frac{m_g^2}{m_M}\right)^{3/2} \frac{g_0^2}{g_m (Z_{rot} Z_{vib})_m} e^{-\epsilon_d/kT} \quad \dots(11.90)$$

where  $m_a$  is the atomic mass,  $m_M$  the molecular mass and  $\epsilon_d$  the dissociation energy.

$$\text{Now } Z_{\text{rot}} = T / 2\theta_r, Z_{\text{vib}} = \frac{1}{1 - e^{-\theta_v/kT}}$$

where  $\theta_r, \theta_v$  are the rotational and vibrational characteristics temperatures.

Further  $m_m = 2m_a$

$$K(P, T) = \frac{P_0^2}{P_m} = \left(\frac{2\pi}{h^2}\right)^{3/2} (kT)^{3/2} \left(\frac{m_a}{2}\right)^{3/2} \left[\frac{1 - e^{-\theta_v/kT}}{T / 2\theta_r}\right] e^{-\epsilon_d/kT} \quad \dots(11.91)$$

$$\text{If we put } \alpha_a = \frac{P_a}{P}, \text{ where } P = P_a + P_m$$

$$K(P, T) = \frac{P(P_a / P)^2}{1 - P_a / P} = \frac{P\alpha_a^2}{1 - \alpha_a} \quad \dots(11.92)$$

**PROBLEMS**

- 11.1** Find the critical temperature, pressure and volume for a gas described by the equation of state  $P(V - b) = RT e^{-a/RTV}$  (Dieterici equation) where  $a$ ,  $b$  are constants.
- 11.2** Find the heat of vaporization of water at a pressure  $1.013 \times 10^5$  Pa, given that
- (i) its boiling point at a pressure  $1.03 \times 10^5$  Pa is  $100^\circ\text{C}$  and at  $1.05 \times 10^5$  Pa it is  $101^\circ\text{C}$ , and
  - (ii) its specific volume upon vaporization at a lower pressure increases from  $1.04 \times 10^{-3}$  to  $1.673 \text{ m}^3/\text{kg}$ .
- 11.3** Given that the critical temperature of hydrogen is  $33.2$  K; its critical pressure is  $1.295 \times 10^6$  Pa and the molar volume in the critical state is  $6.5 \times 10^{-5} \text{ m}^3/\text{mole}$ , find the van der Waal's constants.
- 11.4** Using the data obtained in the preceding problem, find the pressure from van der Waal's equation for (i) a molar volume  $10^{-3} \text{ m}^3/\text{mol}$  at a temperature  $300$  K; and (ii) a molar volume  $10^{-4} \text{ m}^3/\text{mol}$  at a temperature  $35$  K. Compare the results with the pressure of the ideal gas under the conditions of each case.
- 11.5** The density of ice is  $\rho = 0.9 \text{ g/cm}^3$  and its heat of fusion is  $334 \text{ kJ/kg}$ . Find the change in the melting point of ice if the pressure has changed from  $0.098$  to  $0.196 \text{ MPa}$ .



So far we have considered the application of statistical mechanics to the systems in equilibrium when looked at from a microscopic point of view. Details of the interaction processes which bring about the equilibrium were not considered. We shall discuss in this chapter some simple approximate methods for dealing with non-equilibrium processes. To obtain a deeper understanding of the transport phenomena, a more general theory will be given in the next chapter. We shall be mainly concerned with the interactions that take place between atoms and molecules at kinetic energies which are appropriate for conventional thermal energies.

### 12.1 MEAN COLLISION TIME

Let us consider a gas which is dilute. If the gas is not initially in equilibrium, collisions between the molecules bring about the ultimate equilibrium situation. In dilute gases the time between collisions is much greater than the time involved in the collision. Let  $P(t)$  be the probability that a molecule survives a time  $t$  without suffering a collision and  $\gamma dt$  the probability that a molecule suffers a collision between time  $t$  and  $t + dt$ . One can see that  $P(0) = 1$ , and that the probability that a molecule does not suffer a collision in the interval  $t$  to  $t + dt$  is  $1 - \gamma dt$ . Therefore, the probability that a molecule survives a time  $t + dt$  is

$$P(t + dt) = P(t)(1 - \gamma dt) \quad \dots(12.1)$$

Therefore,  $P(t) + \frac{dP(t)}{dt} dt = P(t) - P(t)(\gamma dt)$

or  $\frac{1}{P(t)} \frac{dP(t)}{dt} = -\gamma \quad \dots(12.2)$

Integrating  $\ln P(t) = -\gamma t + \ln C$

or  $P(t) = Ce^{-\gamma t} \quad \dots(12.3)$

Because  $P(0) = C = 1$

therefore  $P(t) = e^{-\gamma t} \quad \dots(12.4)$

Consider now another situation : a molecule survives a time  $t$  without collision, but suffers a collision in the interval  $t$  to  $t + dt$ . The probability of occurrence of such an event is

$$p_1(t) dt = e^{-\gamma t} \gamma dt \quad \dots(12.5)$$

Therefore, the mean time between collisions is

$$\tau = \int_0^{\infty} t p_1(t) dt = \int_0^{\infty} e^{-\gamma t} \gamma t dt$$

Put

$$\gamma t = y$$

$$\text{Therefore } \tau = \frac{1}{\gamma} \int_0^{\infty} e^{-y} y dy = \frac{1}{\gamma} \quad \dots(12.6)$$

or

$$p_1(t) = e^{-t/\tau} \frac{dt}{\tau} \quad \dots(12.7)$$

$$\text{Since } \int_0^{\infty} p_1(t) dt = \int_0^{\infty} e^{-t/\tau} \frac{dt}{\tau} = 1$$

The probability (12.7) is properly normalized.

The mean free path  $l$ —that is the mean distance travelled by a molecule between collisions—is given by

$$l = \langle v \rangle \tau = \frac{\langle v \rangle}{f_A} \quad \dots(12.8)$$

where  $\langle v \rangle$  is the mean velocity of a molecule and  $f_A$  is the collision frequency.

## 12.2 SCATTERING CROSS-SECTION

The effect of the encounter or interaction between two particles is usually described in terms of a collision cross-section.

Consider a beam of particles. The number of particles crossing a unit area perpendicular to the beam per unit item is called the flux  $F$ . If  $n$  is the number of particles per unit volume (Fig. 12.1)

$$F = n \langle v \rangle \quad \dots(12.9)$$

Dimensions of flux are:  $L^{-2} T^{-1}$   $\dots(12.10)$

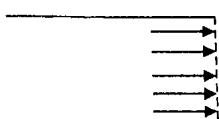


Fig. 12.1

When the beam approaches the target particles some of the particles are deviated by the force field, so that they eventually move away at an angle  $\theta$  with respect to its original direction. The angle  $\theta$  is called the scattering angle. Let  $dF$  be the number of particles scattered per second in a solid angle  $d\Omega$  along a direction given by  $\theta$  and  $\phi$ . The number  $dF$  will obviously be proportional to  $F$  as well as the magnitude of the solid angle  $d\Omega$ .

Therefore  $dF \propto F d\Omega$   
 i.e.  $dF = \sigma(\Omega) F d\Omega = F d\sigma$  ... (12.11)

The constant of a proportionality  $\sigma(\Omega)$  will depend on  $\theta$  and  $\phi$  and is known as the differential cross-section.

We find from Eq. (12.11) that

$$\sigma(\Omega) d\Omega = \frac{dF}{F} = d\sigma \quad \dots (12.12)$$

The differential cross-section, therefore, is a measure of the probability that a particle will be scattered in solid angle  $d\Omega$ .

The total scattering cross-section  $\sigma$ , i.e. the total number of particles deflected in all directions per unit flux per unit time is given by

$$\sigma = \sigma \int \sigma(\Omega) d\Omega \quad \dots (12.13)$$

The total number of particles scattered in all directions per unit time is

$$N = F\sigma \quad \dots (12.14)$$

Dimensions of  $\sigma$  are:  $T^{-1}(L^{-2} T^{-1})^{-1} = L^2$  ... (12.15)

The geometrical meaning of  $\sigma(\Omega)$  is

Number of particles scattered into the solid angle $d\Omega$ per unit time	Number of particles in the incident beam, crossing an area equal to $\sigma(\Omega) d\Omega$ per unit time	... (12.16)
---	---	-------------

Thus, we speak of nuclear cross-sections being of the order of  $10^{-30}$  m<sup>2</sup>, molecular cross-sections of the order of  $10^{-20}$  m<sup>2</sup>, and so on.

Provided that the interaction between the particles is a function of  $r$  only and that processes such as the creation of new particles are not involved, the definition of the differential cross-section as given by Eq. (12.12) is valid, whether the interaction is described by quantum or classical mechanics.

Consider now a particle in a beam of particles incident on a scattering centre (Fig. 12.2).

Let  $b$  be the perpendicular distance between the scattering centre and the velocity of the incident particle.  $b$  is known as the *impact parameter*. Suppose, this particle is scattered at an angle  $\theta$ . Then a particle with an impact parameter  $b + db$  will be scattered through a smaller angle  $\theta - d\theta$ . The particles have azimuthal symmetry. Therefore, all the particles in the annular ring  $2\pi b db$  will be scattered in the solid angle

$$d\Omega = 2\pi \sin\theta d\theta$$

Therefore  $2\pi b F db = 2\pi F \sin\theta d\theta \sigma(\Omega)$  ... (12.17)

or  $\sigma(\Omega) = -\frac{b}{\sin\theta} \frac{db}{d\theta}$  ... (12.18)

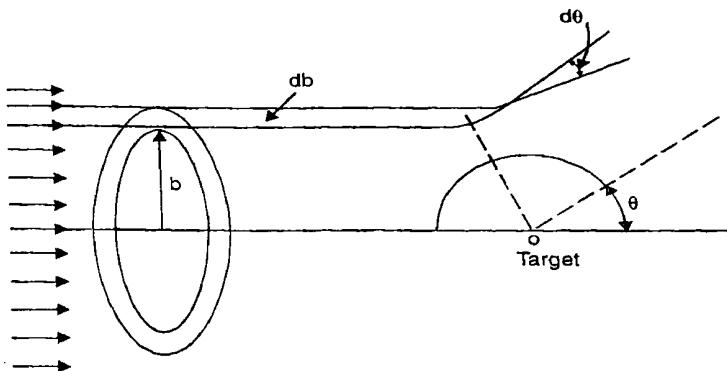


Fig. 12.2

The negative sign is attached because the derivative  $db/d\theta$  is -ve, that is, as  $b$  increases  $\theta$  decreases.

**Example 12.1** A hard sphere of radius  $s$  is advancing towards a sphere of radius  $r$ . Find the differential and total cross-sections.

The sphere of radius  $s$  will get scattered after collision, as shown in Fig. 12.3.

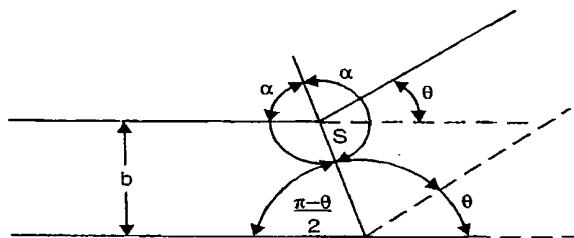


Fig. 12.3

Here the impact parameter

$$b = (s + r) \sin \alpha = (s + r) \sin \frac{\pi - \theta}{2} = (s + r) \cos \frac{\theta}{2} \quad \dots(12.19)$$

$$\text{Therefore } \frac{db}{d\theta} = -\frac{1}{2} (s + r) \sin \frac{\theta}{2} \quad \dots(12.20)$$

$$\begin{aligned} \text{Therefore } \sigma(\Omega) &= \frac{-b}{\sin \theta} \frac{db}{d\theta} = \frac{b(s+r)}{2 \sin \theta} = \frac{b(s+r) \sin \frac{\theta}{2}}{4 \sin \frac{\theta}{2} \cos \frac{\theta}{2}} \\ &= \frac{(s+r)^2}{4} \quad \dots(12.21) \end{aligned}$$

and  $\sigma = \int \sigma(\Omega) d\Omega = \frac{(s+r)^2}{4} \cdot 4\pi = \pi(s+r)^2 \quad \dots(12.22)$

If  $\sigma$  is known, one can readily find the probability  $\gamma$  that a molecule suffers a collision in unit time.

Consider a gas consisting of a certain kind of molecules. Let  $n$  be the mean number of molecules per unit volume. Also let  $\langle v \rangle$  be the mean speed of these molecules and  $\langle V \rangle$  be their mean relative speed.

Suppose we wish to calculate  $\gamma$  of a particular type of molecules in this gas. Let their number per unit volume be  $n_1$ . The flux of this type of molecules, say type 1 molecules incident on any one molecule in a volume element  $d^3r$  is given by

$$F_1 = n_1 \langle \bar{V} \rangle \quad \dots(12.23)$$

The number of these incident molecules scattered per unit time by the target molecule in  $n_1 \langle V \rangle \sigma$ . Hence, the total number of type 1 molecules scattered by all the molecules in the element  $d^3r$  is

$$(n_1 \langle \bar{V} \rangle \sigma)(nd^3r)$$

Therefore collision probability  $\gamma = \frac{1}{\tau}$

$$\begin{aligned} &= \frac{\text{Total number of scattered molecules}}{\text{Total number of molecules present}} \\ &= \frac{(n_1 \langle \bar{V} \rangle \sigma)(nd^3r)}{n_1 d^3 r} = n \langle \bar{V} \rangle \sigma \quad \dots(12.24) \end{aligned}$$

The collision probability  $\gamma$ , therefore, is proportional to the number of molecules per unit volume, to the relative velocity  $\langle \bar{V} \rangle$  and to the cross-section  $\sigma$ .

We know that the mean free path  $l$  is

$$l = \tau \langle \bar{v} \rangle = \frac{\langle v \rangle}{n \langle V \rangle \sigma} \quad \dots(12.25)$$

An approximate value of the ratio  $\frac{\langle v \rangle}{\langle V \rangle}$  can be found as follows:

Consider two different molecules moving with velocities  $v_1$  and  $v_2$ . Their relative velocity is given by

$$V = v_1 - v_2$$

$$\text{Therefore } V^2 = v_1^2 + v_2^2 - 2v_1 \cdot v_2 = v_1^2 + v_2^2 - 2v_1 v_2 \cos \theta$$

where  $\theta$  is the angle between the velocity vectors.

$$\begin{aligned} \text{Therefore } \langle V^2 \rangle &= \langle v_1^2 \rangle + \langle v_2^2 \rangle - 2 \langle v_1 v_2 \cos \theta \rangle \\ &= \langle v_1 \rangle^2 + \langle v_2 \rangle^2 \end{aligned}$$

because  $\theta$  is as likely to be positive as negative for molecules moving in random directions.

If the molecules are identical

$$\langle v_1^2 \rangle = \langle v_2^2 \rangle = \langle v^2 \rangle$$

Therefore  $\langle V^2 \rangle = 2 \langle u^2 \rangle$

and  $\frac{\langle v^2 \rangle}{\langle V^2 \rangle} = \frac{1}{2}$

We approximately take  $\frac{\langle v \rangle}{\langle V \rangle} = \frac{1}{\sqrt{2}}$  and thus

$$l = \frac{1}{\sqrt{2n}\sigma} \quad \dots(12.26)$$

**Example 12.2** Find the mean free path and collision rate for the nitrogen gas at STP. Assume the diameter of the molecule to be  $2 \times 10^{-10}$  m.

At

$$\text{STP, } T = 300 \text{ K, } P = 101.325 \text{ kN/m}^2$$

$$n = \frac{\langle p \rangle}{kT} = \frac{101.325 \times 10^3}{1.38 \times 10^{-23} \times 300} = 24.5 \times 10^{24}/\text{m}^3$$

$$\sigma = \pi d^2 = 3.142 (2 \times 10^{-10})^2 = 12.56 \times 10^{-20} \text{ m}^2$$

Therefore

$$l = \frac{1}{\sqrt{2n}\sigma} = 2.3 \times 10^{-7} \text{ m}$$

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{26 \times 1.66 \times 10^{-27}}} = 500 \text{ m/s}$$

or  $\tau = \frac{1}{\langle v \rangle} = \frac{2.3 \times 10^{-7}}{500} = 4.6 \times 10^{-10} \text{ s}$

and the collision rate  $f_A = \frac{1}{\tau} = 2.2 \times 10^9/\text{s}$

## 12.3 VISCOSITY

Consider a gas enclosed between two plates (Fig. 12.4). Let the distance between the plates be  $L$ . Suppose the lower plate at  $z = 0$  is stationary and the upper at  $z = L$  is moving in the  $x$ -direction with a constant velocity  $u_0$ . To a good approximation we can assume that the layers of the gas close to the plates will have the velocities of the plates. Thus, the lowest layer will have velocity  $u_x = 0$ , and the topmost  $u_x = u_0$ . The layers between the plates will have velocities in the increasing order of magnitude as shown in the figure. This is obviously a non-equilibrium situation.

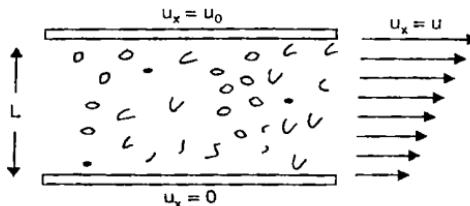


Fig. 12.4

An internal friction in gases—viscosity—is caused by the transport of molecules moving across the direction of motion of the gas layers having different velocities. As a result of thermal motion, the molecules go over from one layer to another, transferring their momentum from one layer to another. As a result of the exchange of molecules between the layers moving with different velocities, the momentum of the faster moving layers decreases, while that of the slower moving layer increases. This is the essence of the mechanism of appearance of the internal friction force between the layers. Every layer in the gas exerts a tangential force on the layer above it tending to reduce its drift velocity. There is, thus,

a gradient of drift velocity,  $\frac{du_x}{dz}$ , superimposed on the random motion of the molecules.

Let  $A$ ,  $Z$ ,  $B$  be the three planes, each of unit area, situated in a gas (Fig. 12.5). Suppose that the separation between the planes is such that  $AZ = ZB = l$  (mean free path). Let the molecules have velocities  $u_x(Z+l)$  and  $u_x(Z-l)$  at  $A$  and  $B$ , respectively. Since the molecules moving downwards have on an average their last collision at  $A$ , their drift velocity at the moment of crossing the plane  $Z$  will be  $u_x(Z-l)$ . Since the molecular velocities are in random direction, roughly one-third of them will be moving in the  $z$ -direction. Half of these, that is  $\frac{1}{6}$  of the molecules will be moving

downwards and  $\frac{1}{6}$  upwards. As the

molecules cross the plane  $z$ , molecules below the plane gain momentum while those above, lose it. Since the force acting on a system is equal to the rate of change of momentum, the gas above the plane is acted upon by a force due to gas below the plane.

The momentum in the  $x$ -direction transported per unit time across  $Z$ , in the upward direction is  $\frac{1}{6} n \langle u_z \rangle m u_x (z-l)$  and that in the downward

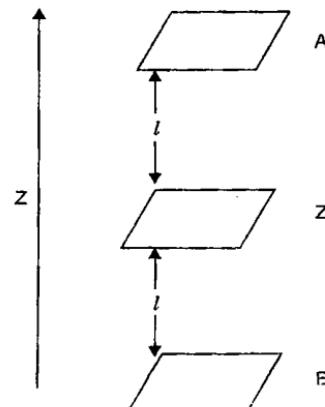


Fig. 12.5

direction is  $\frac{1}{6} n \langle u_z \rangle m u_x (z + l)$ , where  $n$  is the number of molecules per unit volume,  $\langle u_z \rangle$  is the mean velocity in the  $z$ -direction and  $m$  is the mass of a molecule.

The net transport of momentum per unit time, per unit area, from below to above the plane  $Z$  is

$$\begin{aligned} F_{zx} &= \left( \frac{1}{6} n \langle u_z \rangle m u_x (z - l) \right) - \left( \frac{1}{6} n \langle u_z \rangle m u_x (z + l) \right) \\ &= \frac{1}{6} n \langle u_z \rangle m [u_x(z - l) - u_x(z + l)] \end{aligned} \quad \dots(12.27)$$

Expanding by Taylor's theorem, we have

$$\begin{aligned} F_{zx} &= \frac{1}{6} n \langle u_z \rangle m \left[ u_x(z) - \frac{\partial u_x}{\partial z} l - u_x(z) - \frac{\partial u_x}{\partial z} l \right] \\ F_{zx} &= \frac{1}{6} n \langle u_z \rangle m \left[ -2 \frac{\partial u_x}{\partial z} l \right] = -\frac{1}{3} n \langle u_z \rangle m l \frac{\partial u_x}{\partial z} \\ &= \eta \frac{\partial u_x}{\partial z} \end{aligned}$$

where  $\eta = \frac{1}{3} n \langle u_z \rangle m l = \frac{1}{3} \rho \langle u_z \rangle l$  ...(12.28)

is called the *coefficient of viscosity* of the gas.

Since the calculation is over-simplified, the factor  $\frac{1}{3}$  should not be trusted too much. A detailed calculation considering the gas of hard sphere molecules results into the following relation:

$$\eta = \frac{1}{2} \rho \langle u \rangle l \quad \dots(12.29)$$

The relation (12.28) has some interesting features.

Taking into account the Maxwell distribution, we can replace  $u$  by  $\sqrt{\frac{8kT}{m}}$  and  $l$  by Eq. (12.26). We thus have

$$\begin{aligned} \eta &= \frac{1}{3} \rho \sqrt{\frac{8kT}{m}} \cdot \frac{1}{\sqrt{2\pi\sigma}} = \frac{1}{3} mn \sqrt{\frac{8kT}{\pi m}} \cdot \frac{1}{\sqrt{2\pi\sigma}} \\ &= \frac{1}{3\sqrt{2}\sigma} \sqrt{\frac{8kTm}{\pi}} = \frac{1}{3\sqrt{2}\pi^{3/2}d^2} \cdot (8kTm)^{1/2} \quad \dots(12.30) \end{aligned}$$

This relation shows that:

- (i)  $\eta$  is independent of  $n$ , that is of the number of molecules.
- (ii) smaller the size of the molecule, larger is the coefficient of viscosity and

(iii)  $\eta$  increases with temperature.

These results seem to be somewhat extraordinary as they give a big jolt to our intuitive expectations. One would expect the viscous resistance to increase, if the number of molecules and their size increases. Further, in the case of liquids, the viscosity decreases rapidly with temperature. However, the three conclusions stated above were confirmed experimentally by Maxwell. This apparently extraordinary behaviour can be explained as follows.

It is indeed true that by increasing the number of molecules, more molecules will be available to transport momenta from one plane to another; but then the mean free path will proportionately be reduced and the net rate of momentum transfer will remain unchanged.

Regarding the temperature dependence of  $\eta$ , we see from Eq. (12.30) that it varies as  $T^{1/2}$ . This is because we have treated molecules as hard spheres and have assumed  $\sigma = \pi d^2$ . In reality  $\eta$  increases more rapidly than  $T^{1/2}$ . This can easily be understood if we note that  $\sigma$  depends on the mean relative speed of the molecules which, in turn, depends upon the temperature. With increasing temperature  $\sigma$  decreases and, hence,  $\eta$  increases more rapidly than  $T^{1/2}$ . In liquids, however, momentum transfer across a plane occurs by direct forces between the molecules on adjacent sides of the plane and, hence, depends upon  $n$  which decreases with increasing temperature. This results into the decrease of viscous resistance with temperature.

## 12.4 ELECTRICAL CONDUCTIVITY

A simple treatment of electrical conductivity is given in this section.

If a small uniform electric field is applied to a system containing charged particles which are free to move, the particles will be accelerated in the direction of the field.

$$\text{Now} \quad j \propto E$$

$$\text{Therefore} \quad j = \sigma_{el} E$$

...(12.31)

The constant of proportionality  $\sigma_{el}$  is called the *electrical conductivity* of the system.

If  $n$  is the mean number of charged particles per unit volume and  $\langle v \rangle$  is the mean velocity in the field direction, the mean number of particles crossing a unit area per unit time perpendicular to the direction of the field is  $n \langle v \rangle$  and, hence,

$$j = ne \langle v \rangle \quad \dots(12.32)$$

where  $e$  is the charge carried by each particle.

$$\text{Now} \quad \langle v \rangle = a\tau$$

...(12.33)

where  $a$  is the acceleration and  $\tau$  the collision time.

Therefore  $\langle v \rangle = \frac{eE}{m} \tau$  (because  $ma = eE$ ) ... (12.34)

and  $j = \frac{ne^2}{m} \tau E$  ... (12.35)

Therefore  $\sigma_{el} = \frac{ne^2}{m} \tau$  ... (12.36)

In the case of the electron gas in metals, in which the electrons are scattered by atoms of solids, we will assume that only electrons at the Fermi level are thermally excited. Such electrons will have velocities

$$v_F = \left( \frac{2\epsilon_F}{m} \right)^{1/2}$$

If mean free path is  $l_F$ ,  $\tau = \frac{l_F}{v_F}$ .

and  $\sigma_{el} = \frac{ne^2}{m} \frac{l_f}{v_F}$  ... (12.37)

## 12.5 THERMAL CONDUCTIVITY

Consider a system in which the temperature is a function of, say,  $z$ -coordinate. Since the temperature is not uniform, the energy in the form of heat will flow from the region of higher to that of lower temperatures. If the temperature gradient  $\frac{dT}{dz}$  is not too large, the heat flowing per unit area perpendicular to  $z$ ,  $Q_z$  will be proportional to the temperature gradient

$$Q_z \propto \frac{dT}{dz}$$

$$Q_z = -K \frac{dT}{dz} \quad \dots (12.38)$$

Note the negative sign, which is self-explanatory.  $K$  is called the coefficient of thermal conductivity of the substance.

As explained in the preceding section, if there are  $n$  molecules per unit volume, roughly one-third of them will be moving along the  $z$ -direction.

Half of these,  $\frac{1}{6}n$  molecules, will have, on an average, mean velocity  $\langle v \rangle$  in the  $+z$  direction and the other half will have the same velocity in the  $-z$  direction. Consider a unit area in a plane  $z = \text{constant}$ . In the elementary theory of transport, a molecule is assumed to take up the properties of the gas in the vicinity of its last collision. Assume two parallel planes  $A$  and  $B$  as shown in Fig. 12.6, each at a distance  $l$  from the plane  $z = \text{constant}$ .

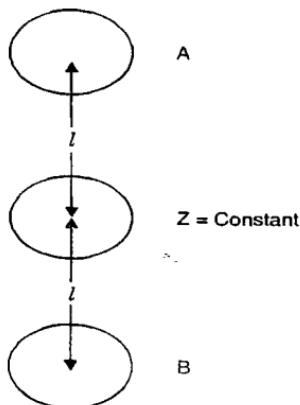


Fig. 12.6

If  $\frac{dT}{dz} < 0$  the molecules coming from A and crossing the area in the plane  $z = \text{constant}$ , will have less mean energy ( $\epsilon_1$ ) than that ( $\epsilon_2$ ) of molecules coming from B. The result is net transport of energy from the region below to that above it.

Therefore

$$\begin{aligned}
 Q_z &= \frac{1}{6} n \langle v \rangle (\epsilon_2 - \epsilon_1) \\
 &= \frac{1}{6} n \langle v \rangle \left( -\frac{\partial \epsilon}{\partial z} \right) z l \\
 &= \frac{1}{3} n \langle v \rangle \left( -\frac{\partial \epsilon}{\partial T} \right) \left( \frac{\partial T}{\partial z} \right) \\
 &= -\frac{1}{3} n \langle v \rangle l c \frac{\partial T}{\partial z}
 \end{aligned} \quad \dots(12.39)$$

where  $c$  is the specific heat per molecule  $\frac{\partial \epsilon}{\partial T}$ .

Comparison of Eq. (12.38) with Eq. (12.39) gives

$$K = \frac{1}{3} n \langle v \rangle l c \quad \dots(12.40)$$

The considerations could be extended to the calculation of thermal conductivity of a metal, when heat is predominantly transferred by conduction electrons. As in the case of electrical conductivity, we assume that only electrons at the Fermi level participate in the transportation of the energy, their velocity and the mean free path being  $v_F$  and  $l_F$  respectively.

$$\text{Therefore } Q_z = -\frac{1}{3} n v_F l_F \left( \frac{\partial \epsilon}{\partial T} \right) \left( \frac{\partial T}{\partial z} \right) \quad \dots(12.41)$$

where  $\frac{\partial \epsilon}{\partial T}$  is the average specific heat per electron and is equal to

$$\frac{\pi^2 k^2 T}{2 \epsilon_F} \quad [\text{see Eq. (10.77)}]$$

$$\text{Therefore } K = \frac{1}{3} n v_F l_F \frac{\pi^2 k^2 T}{2 \epsilon_F}$$

$$\text{Substituting for } \epsilon_F \quad K = \frac{1}{3} \frac{n l_F \pi^2 k^2 T}{m v_F} \quad \dots(12.42)$$

Consider now the ratio of thermal to electrical conductivities

$$\begin{aligned} \frac{K}{\sigma_{el}} &= \frac{n l_F \pi^2 k^2 T}{3 m v_F} \cdot \frac{m v_E}{n e^2 l_F} \\ &= \frac{\pi^2 k^3 T}{3 e^2} \end{aligned} \quad \dots(12.43)$$

Thus the ratio depends only on the temperature  $T$  and is independent of the mass of the electrons, their number density or their collision time.

The above result Eq. (12.43) is known as Wiedemann-Franz law. The ratio  $\frac{K}{\sigma_T} = \frac{\pi^2}{3} \left( \frac{k}{e} \right)^2$  is known as the *Lorenz number*.

## 12.6 THERMIONIC EMISSION

We know that metals emit electrons when they are heated to a high temperature. The phenomenon is called *thermionic emission*. Since the electron emission does not take place spontaneously, electrons in the metal may be considered to be inside a potential well created by metallic ions. Suppose the energy of the electrons in the well is  $-W$ . Then only those electrons whose kinetic energy  $\epsilon_n$  associated with the motion normal to a surface of the metal, is greater than  $W$  can escape through the surface barrier. If the surface lies in the  $yz$ -plane, the electrons which

have energy  $\epsilon_x = \frac{1}{2} m u_x^2 > W$  will escape through the surface.

The number of electrons per unit volume with momenta between  $p$  and  $p + dp$  is

$$N(p)dp = \frac{2}{h^3} dp_x dp_y dp_z f(\epsilon)$$

where  $f(\epsilon)$  is the distribution function.

Therefore, the number of electrons leaving per unit area per unit time is

$$N = \int N(p) dp v_x$$

$$\text{i.e. } N = \frac{2}{h^3} \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \int_{\sqrt{2mW}}^{\infty} dp_x \frac{v_x}{e^{\beta \left( \frac{p_x^2 + p_y^2 + p_z^2}{2m} - \epsilon_F \right)} + 1} \quad \dots(12.44)$$

$$= \frac{2}{mh^3} \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \int_{\sqrt{2mW}}^{\infty} \frac{p_x dp_x}{e^{\beta \left( \frac{p_x^2 + p_y^2 + p_z^2}{2m} - \epsilon_F \right)} + 1} \quad \dots(12.45)$$

Since  $W$  is of the order of 1 to 5 eV, and only those electrons whose energies are in excess of  $W$  contribute to the emission, we may ignore the term unity in the denominator.

$$\begin{aligned} \text{Therefore } N &= \frac{2}{mh^3} \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \int_{\sqrt{2mW}}^{\infty} e^{-\beta \left( \frac{p_x^2 + p_y^2 + p_z^2}{2m} - \epsilon_F \right)} p_x dp_x \\ &= \frac{2e^{\beta \epsilon_F}}{mh^3} \int_{-\infty}^{\infty} e^{-\beta p_y^2/2m} dp_y \int_{-\infty}^{\infty} e^{-\beta p_z^2/2m} dp_z \times \\ &\quad \int_{\sqrt{2mW}}^{\infty} e^{-\beta p_x^2/2m} p_x dp_x \\ &= \frac{2e^{\beta \epsilon_F}}{mh^3} \sqrt{\frac{2\pi m}{\beta}} \cdot \sqrt{\frac{2\pi m}{\beta}} \cdot \frac{m}{\beta} e^{-\beta W} \\ &= \frac{4\pi m}{\beta^2 h^3} e^{\beta(\epsilon_F - W)} \end{aligned} \quad \dots(12.46)$$

The current density  $j$  carried by these electrons is

$$\begin{aligned} j &= Ne = \frac{4\pi m e_0 k^2 T^2}{h^2} e^{\beta(\epsilon_F - W)} \\ &= \frac{4\pi m e k^2 T^2}{h^3} e^{-\beta \phi} \end{aligned} \quad \dots(12.47)$$

where  $e$  is the charge on the electrons and  $\phi = W - \epsilon_F$ . The factor  $\phi$  is generally referred to as the *work function* of the metal. It represents the energy necessary to remove from a metal an electron that has an energy equal to the Fermi energy.

Equation (12.47) is known as *Richardson-Dushman* equation for thermionic emission.

## 12.7 PHOTOELECTRIC EFFECT

When light radiation of sufficient energy falls on a metal, electrons are ejected from it. This is the phenomenon of *photoelectric emission*. In this case a conduction electron absorbs a photon of energy  $h\nu$  from the incoming beam. If the energy is high enough, the electron escapes the surface.

We may assume that components of momentum  $p_y$ ,  $p_z$  parallel to the surface remain unchanged. For the electron to escape from the metal,  $p_x$  has to satisfy the condition

$$\frac{p_x^2}{2m} \geq W - h\nu \quad \dots(12.48)$$

The flux of electrons will depend upon the probability of absorption of a photon. Let this probability be  $a$ , the flux is given by

$$N = \frac{2a}{mh^3} \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \int_{\sqrt{2m(W-h\nu)}}^{\infty} \frac{p_x dp_x}{e^{\beta\left(\frac{p_x^2+p_y^2+p_z^2}{2m}-\epsilon_F\right)} + 1} \quad \dots(12.49)$$

Integration over  $p_y$  and  $p_z$  may be carried out by changing over to the corresponding polar coordinates  $(p', \phi)$ .

$$\begin{aligned} \text{Therefore } n &= \frac{2a}{mh^3} \int_{\sqrt{2m(W-h\nu)}}^{\infty} p_x dp_x \int_{p'=0}^{\infty} \frac{2\pi p' dp'}{e^{\beta\left(p'^2/2m+p_x^2/2m-\epsilon_F\right)} + 1} \\ &= \frac{4\pi a}{h^3 p} \int_{\sqrt{2m(W-h\nu)}}^{\infty} p_x dp_x \ln \left[ \frac{1}{1+e^{\beta\left(\epsilon_F-\frac{p_x^2}{2m}\right)}} \right] \end{aligned} \quad \dots(12.50)$$

or in terms of energy

$$N = \frac{4\pi am}{h^3 \beta} \int_{W-h\nu}^{\infty} \ln \left[ 1 + e^{\{\beta(\epsilon_F - \epsilon_x)\}} \right] d\epsilon_x \quad \dots(12.51)$$

Changing to a new variable

$$y = \beta(\epsilon_x - W + h\nu) \quad \dots(12.52)$$

Eq. (12.51) changes to

$$\begin{aligned} N &= \frac{4\pi am}{h^3 \beta^2} \int_0^{\infty} \ln \left[ 1 + e^{\beta\left(\epsilon_F - \frac{4}{\beta}W + h\nu\right)} \right] dy \\ &= \frac{4\pi am}{h^3 \beta^2} \int_0^{\infty} \ln \left[ 1 + e^{\{\beta(h\nu - \phi) - y\}} \right] dy \end{aligned} \quad \dots(12.53)$$

where  $\phi = W - \epsilon_F$  is the work function.

The current density, therefore, is

$$J = Ne = \frac{4\pi ame}{h^3 \beta^2} \int_0^{\infty} \ln \left[ 1 + e^{(\delta-y)} \right] dy \quad \dots(12.54)$$

where  $\delta = \beta(hv - \phi)$

Integrating by parts

$$\begin{aligned} j &= \frac{4\pi ame}{h^3 \beta^2} \left[ [y \ln(1 + e^{(\delta-y)})]_0^\infty + \int_0^\infty \frac{y}{e^{y-\delta} + 1} dy \right] \\ &= \frac{4\pi ame}{h^3 \beta^2} \int_0^\infty \frac{y}{e^{y-\delta} + 1} dy = \frac{4\pi ame}{h^3 \beta^2} f(e^\delta) \quad \dots(12.55) \end{aligned}$$

where the integral has been represented as a function of  $e^\delta$ , i.e.  $f(e^\delta)$

If  $hv - \phi \gg kT$ ,  $e^\delta \gg 1$  and the function  $f(e^\delta) \approx \frac{\delta^2}{2}$

then  $j = \frac{4\pi ame}{h^3 \beta^2} \frac{\delta^2}{2} = \frac{2\pi ame}{h^3} (hv - \phi)^2 \quad \dots(12.56)$

Let  $\phi = hv_0$

then  $j = \frac{2\pi ame}{h} (v - v_0)^2$

$v_0$  is called the *threshold frequency*.

We, thus, see that when the energy of the light quantum is much greater than the work function of the metal, the current is independent of temperature.

If, on the other hand,  $e^\delta \ll 1$ ,  $f(e^\delta) \approx e^\delta$ , then

$$\begin{aligned} j &= \frac{4\pi ame}{h^3 \beta^2} e^\delta \\ &= \frac{4\pi amek^2 T^2}{h^3} e^{\beta(hv - \phi)} \quad \dots(12.57) \end{aligned}$$

Compare this with the thermionic current density (12.47)

When  $hv = \phi$ ,  $\delta = 0$  and  $f(e^\delta) = \frac{\pi^2}{12}$

$$j = \frac{\pi^2 amek^2 T^2}{3h^3} \quad \dots(12.58)$$

The agreement between the experimental values and the theoretical values calculated from the above formula is found to be excellent.

## 12.8 MOLECULAR COLLISIONS

Let us first calculate the mean number of impacts between the molecules of a gas and a unit area of the wall of the container per unit time.

Consider an element of unit area on one of the walls normal to say  $x$ -axis. Let  $f(v)d^3v$  be the probability that the molecules will have velocity between  $v$  and  $v + dv$ , then

$$\int_{a|_v} f(v) d^3 v = 1 \quad \dots(12.59)$$

The number of such molecules per unit volume is  $n f(v) d^3 v$ , where  $n = \frac{N}{V}$ . Of these, those which are in the cylindrical volume of base of unit area and height  $v_x$  will strike the element of area per unit time. The number of such molecules is

$$dv = v_x n f(v) d^3 v \quad \dots(12.60)$$

The total number of impacts of gas molecules per unit area of the wall per unit time can be found by integrating Eq. (12.60) over all velocities; over  $v_y$  and  $v_z$  from  $-\infty$  to  $\infty$  and over  $v_x$  from 0 to  $\infty$  since, when  $v_x < 0$ , the molecules are moving away from the wall and do not collide with it.

Therefore, the number of impacts per unit area per unit time is

$$v = n \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty v_x f(v) dv_x dv_y dv_z \quad \dots(12.61)$$

In order to find the kinetic pressure exerted by the gas on the walls, we have to consider the total normal momentum imparted by the gas molecules per unit time per unit area of the wall. On collision, the normal component of the momentum of the particles changes from  $p_x$  to  $-p_x$ . The normal momentum imparted to the wall by the molecules whose velocities lie between  $v$  and  $v + dv$  is, therefore,  $2p_x v_x n f(v) d^3 v$ . Hence, the pressure  $P$  is

$$P = 2n \int_{v_y=-\infty}^\infty \int_{v_z=-\infty}^\infty \int_{v_x=0}^\infty p_x v_x f(v) dv_x dv_y dv_z \quad \dots(12.62)$$

Or, since  $p_x v_x$  is an even function of  $v_x$

$$P = n \int_{v_y=-\infty}^\infty \int_{v_z=-\infty}^\infty \int_{v_x=0}^\infty p_x v_x f(v) dv_x dv_y dv_z \quad \dots(12.63)$$

$$p = n \int_{a|_v} (p_x v_x) f(v) d^3 v \quad \dots(12.64)$$

$$= n \langle p_x v_x \rangle \quad \dots(12.65)$$

$$= n \langle p_v \cos^2 \theta \rangle \quad \dots(12.66)$$

$$= \frac{1}{3} \langle npv \rangle \quad \dots(12.67)$$

**Example 12.3** Find the average number of impacts of molecules of a Maxwell-Boltzmann gas on unit area of the wall per unit time.

Now

$$dv = n \left( \frac{m}{2\pi k T} \right)^{3/2} e^{-\beta \frac{m}{2}(v_x^2 + v_y^2 + v_z^2)} v_x dv_x dv_y dv_z \quad \dots(12.68)$$

Therefore, total number of impacts

$$\begin{aligned} v &= n \left( \frac{m}{2\pi kT} \right)^{3/2} \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z \int_0^{\infty} e^{-\beta \frac{m}{2}(v_x^2 + v_y^2 + v_z^2)} v_x dv_x \\ &= n \left( \frac{m}{2\pi kT} \right)^{3/2} \sqrt{\frac{2\pi}{\beta m}} \sqrt{\frac{2\pi}{\beta m}} \int_0^{\infty} e^{-\frac{\beta m v_x^2}{2}} v_x dv_x \end{aligned}$$

$$= n \left( \frac{m}{2\pi kT} \right)^{3/2} \cdot \frac{2\pi}{\beta m} \cdot \frac{1}{\beta m} = n \sqrt{\frac{kT}{2\pi m}} \quad \dots(12.69)$$

$$= \frac{P}{\sqrt{2\pi m kT}} \text{ (because } P = nkT) \quad \dots(12.70)$$

**Example 12.4** Calculate the number of impacts per unit time per unit area of the wall made by the molecules of an *MB* gas, for which the angles between the direction of the velocity of the molecules and the normal to the surface lie between  $\theta$  and  $\theta + d\theta$ .

It is convenient to use spherical polar coordinates in this case.

Let  $x$  be the polar axis.

Therefore  $v_x = v \cos \theta$

$$\begin{aligned} \text{or } dv &= n \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} \int_0^{2\pi} e^{-\frac{\beta m v^2}{3}} v \cos \theta v d\theta v \sin \theta dv d\phi \\ &= 2\pi n \left( \frac{m}{2\pi kT} \right)^{3/2} \left( \int_0^{\infty} e^{-\beta m v^2 / 2} v^3 dv \right) \sin \theta \cos \theta d\theta \\ &= 2\pi n \left( \frac{m}{2\pi kT} \right)^{3/2} \frac{2}{\beta^2 m^2} \sin \theta \cos \theta d\theta \\ &= n \left( \frac{2kT}{m\pi} \right)^{1/2} \sin \theta \cos \theta d\theta \quad \dots(12.71) \end{aligned}$$

**Example 12.5** Find the number of impacts per unit time per unit area of a wall in an electron gas at absolute zero of temperature.

The number of electrons per unit volume with momenta between  $p$  and  $p + dp$  and at an angle with the normal to the wall between  $\theta$  and  $\theta + d\theta$  is

$$\frac{2.2\pi p d\theta p \sin \theta dp}{h^3} \quad \dots(12.72)$$

Therefore, the number of impacts per unit time

$$\begin{aligned} &= \int_0^{\pi/2} d\theta \int_0^{p_f} dp \frac{2.2\pi p^2 \sin \theta}{h^3} v \cos \theta \\ &= \frac{4\pi}{mh^3} \int_0^{\pi/2} d\theta \int_0^{p_f} p^3 \sin \theta \cos \theta dp \end{aligned}$$

$$= \frac{4\pi}{mh^3} \cdot \frac{1}{2} \cdot \frac{p_F^4}{4} = \frac{nh}{2m} \left( \frac{3N}{8\pi V} \right)^{4/3} \quad \dots(12.73)$$

## 12.9 EFFUSION

Suppose a small hole is made in the wall of the container. The molecules of the gas within the container will emerge through the hole. This process is known as *effusion*.

The number of molecules emerging through the hole is the same as the number of molecules which would strike the same element of area if the hole is not made in the wall. This number is given by

$$\dot{N} = n \int_{v_x=-\infty}^{\infty} \int_{v_y=-\infty}^{\infty} \int_{v_z=0}^{\infty} v_x f(v) dv_x dv_y dv_z \quad \dots(12.74)$$

or in spherical polar coordinates

$$\begin{aligned} \dot{N} &= n \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi/2} \int_{v=0}^{\infty} v \cos \theta f(v) v^2 \sin \theta d\theta d\phi dv \\ &= n 2\pi \frac{1}{2} \int_0^{\infty} v^3 f(v) dv \end{aligned} \quad \dots(12.75)$$

$$= n\pi \frac{1}{4\pi} \int_0^{\infty} v f(v) 4\pi v^2 dv \quad \dots(12.76)$$

Since  $f(v) 4\pi v^2 dv$  is the probability that the molecules will have velocity between  $v$  and  $v + dv$ ,

$$\dot{N} = \frac{1}{4} n \langle v \rangle \quad \dots(12.77)$$

The result holds independently of the statistics obeyed by the particles and is thus, valid for BE, FD and MB gases.

If the gas obeys MB statistics

$$\langle v \rangle = \left( \frac{8kT}{\pi m} \right)^{1/2}$$

and

$$\dot{N} = \frac{1}{4} n \left( \frac{8kT}{\pi m} \right)^{1/2} = \frac{P}{\sqrt{2\pi m k T}} \quad \dots(12.78)$$

Isotopes of different masses have different rates of flow out of the hole. Thus, if the enclosure contains isotopes  ${}^3\text{He}$  and  ${}^4\text{He}$

$$\frac{\dot{N}_3}{\dot{N}_4} = \frac{n_3}{n_4} \left( \frac{m_4}{m_3} \right)^{1/2} \quad \dots(12.79)$$

An interesting example of the application of the theory developed above concerns the rate of evaporation from a surface. At low vapour pressure

$$\begin{aligned}
 \text{Number of molecules} &= \text{Number striking} \\
 \text{evaporating from unit} & \quad \text{unit area} \\
 \text{area per second} & \quad \text{per second} \\
 &= \frac{1}{4} n \langle v \rangle \\
 &= \frac{P \langle v \rangle}{4kT} \quad \dots(12.80)
 \end{aligned}$$

This provides a simple method for estimating the rate of evaporation at a given pressure.

**Example 12.6** Find the rate of evaporation of tungsten at 2000 K, its vapour pressure at this temperature being  $6.5 \times 10^{-12}$  torr and its atomic weight 183.8.

Number of atoms evaporating per second is given by

$$\begin{aligned}
 \dot{N} &= \frac{P \langle v \rangle}{4kT} = \frac{P}{4kT} \left( \frac{8kT}{\pi m} \right)^{1/2} = \frac{P}{\sqrt{2\pi m k T}} \\
 P &= 6.5 \times 10^{-12} \times 133.22 \text{ N/m}^2
 \end{aligned}$$

$$\begin{aligned}
 \dot{N} &= \frac{6.5 \times 10^{-12} \times 133.22}{2 \times 3.13 \times 183.8 \times 1.60 \times 10^{-27} \times 1.38 \times 10^{-23} \times 2000} \\
 &= 3.76 \times 10^{12}
 \end{aligned}$$

Therefore, mass evaporating per second

$$\begin{aligned}
 &= 3.76 \times 10^{12} \times 183.8 \times 1.66 \times 10^{-27} \\
 &= 1.15 \times 10^{-12} \text{ kg}
 \end{aligned}$$

## 12.10. DIFFUSION

Diffusion plays an important role in the non-equilibrium theory. We, therefore, present here a very simple form of the theory.

Consider a tube filled with a gas of type, say, B. Suppose molecules of type A are now inserted in the tube at P. Let  $n_A$  be the number of molecules of type A per unit volume. In the equilibrium situation, the molecules A would be uniformly distributed throughout the available volume. The molecules of type A, therefore, will move tending to make the concentration more nearly uniform (Fig. 12.7).

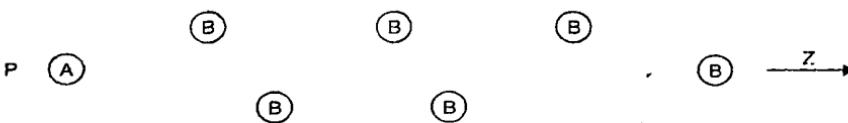


Fig. 12.7

Let  $\Gamma_z$  represent the flux of molecules A, i.e. the number of molecules crossing unit area perpendicular to z-direction per unit time. It would be reasonable to assume that  $\Gamma_z$  is proportional to the concentration gradient of molecules A.

Therefore

$$\Gamma_z \propto \frac{dn_A}{dz}$$

i.e.

$$\Gamma_z = -D \frac{dn_A}{dz} \quad \dots(12.81)$$

The negative sign is self-explanatory. The constant of proportionality D is called the *coefficient of diffusion*.

Equation (12.81) is known as *Fick's law of diffusion*.

We also have the equation of continuity.

$$\nabla \cdot (\rho v) + \frac{\partial \rho}{\partial t} = 0 \quad \dots(12.82)$$

which can be written as

$$\nabla \cdot \Gamma_z + \frac{\partial n_A}{\partial t} = 0 \quad \dots(12.83)$$

Substituting Eq. (12.81) in Eq. (12.83)

$$\frac{\partial n_A}{\partial t} = D \frac{\partial^2 n_A}{\partial z^2} \quad \dots(12.84)$$

This is the *diffusion equation* satisfied by  $n_A$ .

Consider now a unit area in the plane  $Z = Z_0$ , and two other planes at P and P' on either side of it, each at distance l equal to the mean free path (Fig. 12.8). Let  $n_A$  be the concentration at P. Then the concentration at P' will be  $n_A + \frac{\partial^2 n_A}{\partial z^2} 2l$ . The number of molecules coming from P and

crossing the unit area will be (following the arguments of Sec 3)  $\frac{1}{6} \langle v \rangle n_A$  where  $\langle v \rangle$  is the average velocity; whereas that coming from P' and

crossing the same element in opposite direction is  $\frac{1}{6} \langle v \rangle \left( n_A + \frac{\partial n_A}{\partial z} 2l \right)$ .

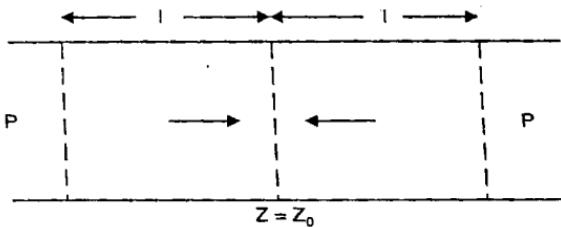


Fig. 12.8

The net flux in the  $+z$  direction is

$$\begin{aligned} P_z &= \frac{1}{6} \langle v \rangle \left( n_A - n_A \frac{\partial n_A}{\partial z} 2l \right) \\ &= -\frac{1}{3} \langle v \rangle l \frac{\partial n_A}{\partial z} \end{aligned} \quad \dots(12.85)$$

Comparing this with Eq. (12.81), we find

$$D = \frac{1}{3} \langle v \rangle l \quad \dots(12.86)$$

For MB gas  $\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$  and from Eq. (12.26)

$$l = \frac{1}{\sqrt{2n\sigma}} = \frac{1}{\sqrt{2\sigma}} \frac{kT}{\langle P \rangle} \quad \dots(12.87)$$

where  $\sigma$  is the scattering cross-section and  $P$  the pressure. Therefore

$$\begin{aligned} D &= \frac{1}{3} \sqrt{\frac{8kT}{\pi m}} \frac{1}{\sqrt{2\sigma}} \frac{kT}{\langle P \rangle} \\ &= \frac{2}{3\sigma\langle P \rangle} \sqrt{\frac{k^3 T^3}{\pi m}} \end{aligned} \quad \dots(12.88)$$

## 12.11 BROWNIAN MOTION

Small macroscopic particles when immersed in liquids are found to exhibit a random type of motion. This was first observed by Robert Brown in 1828 and the phenomenon is known after him as Brownian motion.

It is now known that the source of this motion lies in the incessant and random bombardment of the particles by the molecules of the surrounding liquid. The problem is easily treated by a method due to Langevin.

Consider a particle surrounded by a fluid environment. Suppose, except for the force arising from the molecular bombardment, no other force acts on the particle. The equation of motion of the particle is

$$M \frac{dv}{dt} = F(t) \quad \dots(12.89)$$

where  $M$  is the mass of particle,  $v(t)$  its velocity and  $F(t)$  the force acting on it as a result of impacts of the fluid molecules. Langevin suggested  $F(t)$  may be written as a sum of two parts: (i) a steady part,  $-\alpha Mv$  which represents the viscous drag on the particle and (ii) a fluctuating part  $\beta(t)M$  which over long intervals of time averages out to zero. Thus

$$M \frac{dv}{dt} = -\alpha Mv + \beta(t)M \quad \dots(12.90)$$

$$\text{i.e. } \frac{d\langle v \rangle}{dt} = -\alpha \langle v \rangle + \beta(t) \quad \dots(12.91)$$

Taking the ensemble averages

$$\frac{d\langle v \rangle}{dt} = -\alpha \langle v \rangle + \langle \beta(t) \rangle = -\alpha \langle v \rangle$$

$$\text{Because } \langle \beta(t) \rangle = 0 \quad \dots(12.92)$$

$$\text{Integrating } \langle v \rangle = v(0) e^{-\alpha t} \quad \dots(12.93)$$

This gives the rate at which the drift velocity decays.

$$\text{If } t = \tau = \frac{1}{\alpha}, \langle v(t) \rangle = \frac{1}{e} v(0)$$

The time  $\tau = 1/\alpha$  is known as the *relaxation time*.

$$\text{Therefore } \langle v(t) \rangle = v(0) e^{-t/\tau} \quad \dots(12.94)$$

Let us construct the scalar product of (12.91) with the instantaneous position  $r$  of the particle, as

$$r \cdot \frac{dv}{dt} = -\alpha r \cdot \mathbf{V} + r \beta(t) \quad \dots(12.95)$$

Taking the ensemble averages

$$\left\langle r \cdot \frac{dv}{dt} \right\rangle = -\alpha \langle r \cdot v \rangle + \langle r \cdot \beta(t) \rangle \quad \dots(12.96)$$

Now  $\langle r \cdot \beta(t) \rangle = 0$  because there is no correlation between the position  $r(t)$  of the particle and the fluctuating force  $\beta(t)$

$$r \cdot v = \frac{1}{2} \frac{dr^2}{dt}$$

$$\text{and } r \cdot \frac{dv}{dt} = \frac{1}{2} \frac{d^2 r^2}{dt^2} - v^2$$

Therefore, from Eq. (12.96)

$$\frac{d^2 \langle r^2 \rangle}{dt^2} = \alpha \frac{d^2 \langle r^2 \rangle}{dt^2} = 2 \langle v^2 \rangle \quad \dots(12.97)$$

If the particle has attained thermal equilibrium with the molecules of the fluid

$$\frac{1}{2} M \langle v^2 \rangle = \frac{3}{2} kT$$

$$\text{Therefore } \langle v^2 \rangle = \frac{3kT}{M} \quad \dots(12.98)$$

Thus Eq. (12.97) can be written as

$$\frac{d^2}{dt^2} \langle r^2 \rangle + \alpha \frac{d \langle r^2 \rangle}{dt} = \frac{6kT}{m} \quad \dots(12.99)$$

Integrating, and using the boundary condition that  $r = 0$  and  $\dot{r} = 0$  at  $t = 0$

$$\langle r^2 \rangle = \frac{6kT}{m\alpha^2} \{ \alpha t - (1 - e^{-\alpha t}) \} \quad \dots(12.100)$$

$$\text{If } t \ll \frac{1}{\alpha} = \tau$$

$$\begin{aligned} \langle r^2 \rangle &= \frac{6kT}{M\alpha^2} \left[ \alpha t - \left\{ 1 - \left( 1 - \alpha t + \frac{\alpha^2 t^2}{2} \right) \right\} \right] \\ &= \frac{3kT}{M} t^2 = \langle v^2 \rangle t^2 \end{aligned} \quad \dots(12.101)$$

$$\text{Therefore } r = v \cdot t \quad \dots(12.102)$$

which is consistent with Newton's equation of motion.

On the other hand, if  $t \gg \frac{1}{\alpha}$

$$\langle r^2 \rangle = \frac{6kT}{M\alpha^2} \cdot \alpha t = \frac{6kT}{m\alpha} t = \frac{6kT\tau}{M} t \quad \dots(12.103)$$

which corresponds to the Brownian movement.

If the particles are spherical, we can use Stoke's law, viz. the viscous drag force on a particle moving with a velocity  $v$  is  $-6\pi R\eta v$ , where  $R$  is the radius of the particle and  $\eta$  the coefficient of viscosity.

$$\text{Therefore } M\alpha = 6\pi R\eta \quad \dots(12.104)$$

$$\text{Hence } \langle r^2 \rangle = \frac{6kT}{M} t \cdot \frac{M}{6\pi R\eta} = \frac{kT}{\pi R\eta} t \quad \dots(12.105)$$

This equation was originally derived by Einstein. It shows that the squared displacement is linear in time. Experimental studies have confirmed Eq. (12.1) with an accuracy of  $\pm 0.5$  per cent.

Einstein treated Brownian motion on the basis of the so-called 'Random walk problem' and thereby established a relationship between diffusion and the mechanism of molecular fluctuation.

## 12.12 EINSTEIN'S RELATION FOR MOBILITY

We have seen how (sec. 12.10) Fick's law,  $\Gamma_z = -D \frac{dn}{dz}$ , leads to the diffusion equation

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial z^2} \quad \dots(12.106)$$

Suppose now that  $N$  particles are concentrated at  $x = 0$  at  $t = 0$ , i.e.

$$n(x, 0) = N\delta(x) \quad \dots(12.107)$$

where  $\delta(x)$  is the Dirac delta function.

Of the various possible solutions of Eq. (12.106), the one relevant to the present problem is

$$n(x, t) = \frac{N}{(4\pi Dt)^{1/2}} e^{-\frac{x^2}{4Dt}} \quad \dots(12.108)$$

Comparison of this equation with Eq. (12.86), brings out clearly the relationship between the random walk problem and the phenomenon of diffusion.

The mean square value of the displacement is given by

$$\begin{aligned} \langle x^2 \rangle &= \frac{1}{n} \frac{N}{(4\pi Dt)^{1/2}} \int_{-\infty}^{\infty} x^2 e^{-\frac{x^2}{4Dt}} dx \\ &= \frac{1}{(4\pi Dt)^{1/2}} (4Dt)^{3/2} \int_{-\infty}^{\infty} y^2 e^{-y^2} dy \quad \left( \text{because } y^2 = \frac{x^2}{4Dt} \right) \\ &= \frac{4Dt}{\sqrt{\pi}} \cdot 2 \cdot \frac{\sqrt{\pi}}{4} = 2Dt \end{aligned} \quad \dots(12.109)$$

Einstein's expression from the mean square displacement is given by Eq. (12.103) as

$$\langle r^2 \rangle = \frac{6kT}{M\alpha} t \quad \dots(12.110)$$

For the one-dimensional case this will reduce to

$$\langle x^2 \rangle = \frac{2kT}{M\alpha} t \quad \dots(12.111)$$

Comparison between this and Eq. (12.109) gives

$$D = \frac{kT}{M\alpha} \quad \dots(12.112)$$

Suppose that in the case of Brownian motion, in addition to the viscous drag and the fluctuating free force due to molecular bombardment a steady force  $K_0$  acts on the particle. The equation of motion (12.90) now would change to

$$M \frac{dv}{dt} = -\alpha M v + \beta(t) M + K_0$$

$$\text{or} \quad \frac{dv}{dt} = -\alpha v + \beta(t) + \frac{K_0}{M} \quad \dots(12.113)$$

Taking averages

$$\frac{d\langle v \rangle}{dt} = -\alpha \langle v \rangle + \langle \beta(t) \rangle + \frac{K_0}{M}$$

In the steady-state situation  $\frac{d\langle v \rangle}{dt} = 0$

$$\text{therefore} \quad \langle v \rangle = \frac{K_0}{M\alpha} \quad \dots(12.114)$$

Mobility  $\mu$  is defined as the drift velocity per unit force

$$\text{Therefore } \mu = \frac{1}{M\alpha} \quad \dots(12.115)$$

$$\text{Hence } D = kT\mu$$

This is Einstein's relation connecting the coefficient of diffusion with mobility.

If the particle lies under influence of an external electric field  $E$

$$\frac{dv}{dt} = -\alpha \langle v \rangle + \langle \beta(t) \rangle + \frac{eE}{M}$$

$$\text{Therefore } D = \frac{kT}{e} \mu \quad \dots(12.116)$$

This is original form of Einstein's relation.

## PROBLEMS

- 12.1 The gas kinetic of helium is  $1.9 \times 10^{-10}$  m. Find the probability that an atom of helium covers a distance 0.5 mm without collision at 0°C and pressure 100 Pa.
- 12.2 A uniform electric field  $E$  is applied to a dilute gas of molecules containing an ion of mass  $m$  and charge  $e$ . The mean time between collision suffered by the ion is  $\tau$ . Find the mean distance in the direction of the field which the ion travels between collisions. Assume that the component of velocity of the ion in the direction of the field after each collision is zero.
- 12.3 Show that the average energy of thermionic electrons associated with the component normal to the surface of the emitter is  $kT$ . What is the energy associated with the other two components of the motion?
- 12.4 Find the mean free path and gas kinetic radius of hydrogen at temperature 273 K and pressure  $1.01 \times 10^5$  Pa. The coefficient of viscosity of hydrogen is  $n = 8.6 \times 10^{-6}$  Pa.s.
- 12.5 Find the number of collisions with a wall in an extreme relativistic completely degenerate electron gas.
- 12.6 A fine hole is made in the wall of a container filled with a gas at a temperature  $T$ . Find the mean energy of the molecules effusing through the hold. How and why does it differ from the mean translational energy of the molecules in the container?
- 12.7 In a molecular beam experiment, the source contains 50% monatomic hydrogen and 50% diatomic hydrogen at a pressure 0.1 Torr. The gas effuses through a  $0.1 \times 0.2$  mm slit. Find the number of H and  $H_2$  particles leaving the slit.

- 12.8 The amount of sodium chloride effusing out of an enclosure through a small hole of area  $1.6 \times 10^{-6} \text{ m}^2$  at temperature 900 K is  $1.84 \times 10^{-6} \text{ kg/hour}$ . Calculate the vapour pressure of sodium chloride at this temperature.
- 12.9 In one-dimensional Brownian motion, the probability that a particle will move forward is equal to the probability that it will move backwards. Show that  $\langle x \rangle = 0$ ;  $\langle (x - \langle x \rangle)^2 \rangle = Nl^2$  where  $l$  is the length of the step.
- 12.10 Considering a set of particles each of mass  $m$  in sedimentation equilibrium. Obtain the Einstein's equation  $D = \mu kT$ .
- 12.11 Determine the steady-state sedimentation velocity for an aluminium particle of diameter one micron in water at room temperature in the Earth's gravitational field.



We have seen that in classical statistics a complete description of a system in equilibrium is given by the Gibbs distribution, which is uniform in space in the absence of applied fields. In practice, however, we have often to deal with systems that are not in equilibrium. This chapter is devoted to the investigation of non-equilibrium states and processes. The method adopted here is a generalization of the methods of statistical physics.

The study of gas dynamics requires a consideration of the general theory of the transport of molecules, momenta and energy. In the elementary theory, the distribution function of molecules was assumed to depend only on the properties of the walls. However, if the effect of the inter-molecular interactions is to be included in the theory, one has to take note of the fact that, due to interchange of energy and momentum during collisions, an isotropy in the velocity distribution is likely to occur. In a non-equilibrium state, the distribution function is generally different from equilibrium distribution function and depends on time and coordinates even in the absence of applied fields. It is the purpose of the general theory to find how the distribution function is modified when non-equilibrium processes prevail.

### 13.1 DISTRIBUTION FUNCTION

Let us first obtain the equations specifying the change of the distribution function in space and time.

Let  $f(r, v, t)$  be the distribution function, which in the general case of a non-equilibrium system depends on coordinates, velocities and time, be defined in such a way that

$f(r, v, t)d^3r d^3v$  = the mean number of molecules whose positions at time  $t$  are located between  $r$  and  $r + dr$  and have velocities lying between  $v$  and  $v + dv$  in the  $\mu$ -space. ... (13.1)

If the total number of molecules in the volume  $V$  is  $N$

$$N = \int f(r, v, t) d^3r d^3v \quad \dots (13.2)$$

If  $f$  is independent of  $r$ , i.e. the molecules are uniformly distributed in space

$$N = V \int f(r, v, t) d^3v$$

or  $\frac{N}{V} = \eta(r, t) = \int f(r, v, t) d^3v$  ... (13.3)

where  $\eta(r, t)$  is the space density of the particles.

The mean value of a function  $\chi(r, v, t)$  denoting a property of the molecules at time  $t$  and at position  $r$ , will be

$$\begin{aligned}\langle x(r, t) \rangle &= \frac{\int f(r, v, t) \chi(r, v, t) d^3v}{\int f(r, v, t) d^3v} \\ &= \frac{1}{\eta(r, t)} \int f(r, v, t) \chi(r, v, t) d^3v\end{aligned}\quad \dots (13.4)$$

## 13.2 BOLTZMANN TRANSPORT EQUATION

At a point  $r$ , the time rate of change of distribution function, assuming the total number of particles to be conserved, may be caused by the drift of molecules in and out of a volume element and also by collisions among the molecules. We, thus, have

$$\frac{\partial f}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{drift} + \left( \frac{\partial f}{\partial t} \right)_{coll} \quad \dots (13.5)$$

In time  $dt$ ,  $f(r, v, t)$  would change to

$$f(r, dv, v + dv, t + dt)$$

If we neglect collisions and follow along a flow line, by Liouville's theorem

$$f(r + dr, v + dv, t + dt) = f(r, v, t)$$

or  $f(r + dr, v + dv, t + dt) - f(r, v, t) = 0$  ... (13.6)

i.e.  $f(r, v, t) + dr \cdot \text{grad}_r f + dv \cdot \text{grad}_v f$  ... (13.7)

$$+ \frac{\partial f}{\partial t} dt - f(r, v, t) = 0$$

where  $\text{grad } f$  is a vector, whose projections are

$$\text{grad}_r f = \left\{ \frac{\partial f}{\partial x}, \frac{\partial f}{\partial y}, \frac{\partial f}{\partial z} \right\}$$

and  $\text{grad}_v f = \left\{ \frac{\partial f}{\partial v_x}, \frac{\partial f}{\partial v_y}, \frac{\partial f}{\partial v_z} \right\}$

Hence  $\frac{\partial f}{\partial t} = - \frac{\partial r}{\partial t} \cdot \text{grad}_r f - \frac{\partial v}{\partial t} \cdot \text{grad}_v f$  ... (13.8)

This is the kinetic equation proposed by Boltzmann for finding the distribution function  $f$ . To take collisions into account, we have to find an explicit expression for  $\left(\frac{\partial f}{\partial t}\right)_{coll}$ .

### 13.3 RELAXATION APPROXIMATION

In general, the term  $\left(\frac{\partial f}{\partial t}\right)_{coll}$  varies depending on which collisions are taken into consideration. In one class of cases, where the departures from the equilibrium conditions are small, it can be represented as

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = -\frac{f - f_0}{\tau} \quad \dots(13.9)$$

where  $f$  is the non-equilibrium distribution,  $f_0$  is the equilibrium distribution and  $\tau$  is known as the relaxation time.

How can we justify such an assumption?

Consider a gas in the state of equilibrium. If some of the molecules are brought out of their equilibrium state in one way or the other, they return to it as a result of collisions with other molecules in a time  $\tau$ —relaxation time, which is the time needed for the system to return to its equilibrium state. The relaxation time characterizes the intensity of interaction with the “other molecules”. Stronger the interaction, smaller is the relaxation time, and more rapidly does the system gain equilibrium. These considerations can be represented mathematically.

If the deviations from equilibrium are small, we expect the rate of restoring equilibrium to be proportional to the deviation from the equilibrium state, i.e.

$$\left(\frac{\partial f}{\partial t}\right)_{coll} \propto (f - f_0)$$

or 
$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \text{const} \times (f - f_0) = -\frac{f - f_0}{\tau} \quad \dots(13.10)$$

Thus, if  $f = f_0$ ,  $\frac{\partial f}{\partial t} = 0$ .

We can write Eq. (13.10) as

$$\frac{\partial(f - f_0)}{\partial t} = -\frac{f - f_0}{\tau}$$

Integrating  $\ln(f - f_0) = -\frac{t}{\tau} + \text{const}$

Therefore  $f(t) - f_0 = \Delta f = (f(0) - f_0) e^{-\frac{t}{\tau}} \quad \dots(13.11)$

where  $f(0)$  is the value of the non-equilibrium distribution function at the initial instant.

Equation (13.11) shows that the deviation  $\Delta f$  of the distribution function from the equilibrium diminishes exponentially with the time constant  $\tau$ . It is for this reason that  $\tau$  is called the relaxation time.

Thus, in the relaxation time approximation, Boltzmann transport equation takes the form

$$\frac{\partial f}{\partial t} + v \cdot \text{grad}_v f + \mathbf{a} \cdot \text{grad}_v f = -\frac{f - f_0}{\tau} \quad \dots(13.12)$$

**Example 13.1** Show that in the relaxation approximation the mean energy of a particle is the same as in the equilibrium state.

The mean energy is given by

$$\langle \epsilon \rangle = \frac{1}{n} \int \epsilon f d^3 r d^3 v = \frac{m}{2n} \int v^2 f d^3 r d^3 v \quad \dots(13.13)$$

In the steady state  $\frac{\partial f}{\partial t} = 0$ .

Therefore, from Eq. (13.12)

$$f = f_0 - tv \cdot \text{grad}_v f - \tau \mathbf{a} \cdot \text{grad}_v f$$

$$\text{Therefore } \langle \epsilon \rangle = \frac{1}{n} \left[ \int \epsilon f_0 d^3 r d^3 v - \int \epsilon v \cdot \text{grad}_v f d^3 r d^3 v - \int \epsilon \mathbf{a} \cdot \text{grad}_v f d^3 r d^3 v \right]$$

Since the energy is an even function and  $v$  and  $\mathbf{a}$  are odd functions, the contribution of the last two integrals in the bracket is zero.

$$\langle \epsilon \rangle = \frac{1}{n} \int \epsilon f_0 d^3 r d^3 v = \frac{m}{2n} \int v^2 f_0 d^3 r d^3 v \quad \dots(13.14)$$

### 13.4 ELECTRICAL CONDUCTIVITY FROM THE RELAXATION APPROXIMATION

To illustrate the application of Eq. (13.12), we consider here the case of electrical conductivity of a specimen.

Suppose an electrical field  $\mathbf{E}$  is applied to a specimen in the  $z$ -direction. The electrons, therefore, will be moving in the  $z$ -direction with a velocity  $v_z$  and their acceleration will be  $\frac{e\mathbf{E}}{m}$ , where  $e$  is the charge and  $m$  the mass of the electron. In the steady state  $\frac{\partial f}{\partial t} = 0$ .

Therefore, Eq. (13.12) reduces to

$$v_z \frac{\partial f}{\partial z} + \frac{e\mathbf{E}}{m} \frac{\partial f}{\partial v_z} = -\frac{f - f_0}{\tau} \quad \dots(13.15)$$

Hence

$$f = f_0 - \tau \left( v_z \frac{\partial f}{\partial z} + \frac{e\mathbf{E}}{m} \frac{\partial f}{\partial v_z} \right) \quad \dots(13.16)$$

Assuming that  $\frac{f - f_0}{\tau} \ll 1$ , we can replace  $f$  in the brackets by  $f_0$  and write

$$f = f_0 - \tau \left( v_z \frac{\partial f_0}{\partial z} + \frac{eE}{m} \frac{\partial f_0}{\partial v_z} \right) \quad \dots(13.17)$$

Now, the equilibrium distribution function  $f_0$  is a function of the velocity  $v$ , temperature  $T$  and the concentration  $n$ , i.e. of the chemical potential  $\mu$ .

$$\text{Therefore } \frac{\partial f_0}{\partial z} = \frac{\partial f_0}{\partial \mu} \frac{\partial \mu}{\partial z} + \frac{\partial f_0}{\partial T} \frac{\partial T}{\partial z} \quad \dots(13.18)$$

$$\text{and } \frac{\partial f_0}{\partial v_z} = \frac{\partial f_0}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial z} = m v_z \frac{\partial f_0}{\partial \varepsilon} \quad \left( \text{because } \varepsilon_z = \frac{1}{2} m v_z^2 \right) \quad \dots(13.19)$$

Since, the temperature and the carrier concentration does not change with  $z$ , we have

$$\frac{\partial T}{\partial z} = 0 \text{ and } \frac{\partial \mu}{\partial z} = 0$$

$$\text{Therefore } f = f_0 - \frac{\tau e E}{m} \cdot m v_z \frac{\partial f_0}{\partial \varepsilon} = f_0 - \tau e E v_z \frac{\partial f_0}{\partial \varepsilon} \quad \dots(13.20)$$

The electric current density is given by

$$\begin{aligned} j &= \int e v_z f d^3 v \\ &= e \int v_z f_0 d^3 v - \tau e^2 E \int v_z^2 \frac{\partial f_0}{\partial \varepsilon} d^3 v \end{aligned} \quad \dots(13.21)$$

Since  $f_0$  is an even function of the velocity, the first integrand being odd, vanishes

$$\text{Therefore } j = -\tau e^2 E \int v_z^2 \frac{\partial f_0}{\partial \varepsilon} d^3 v \quad \dots(13.22)$$

Assuming the equilibrium distribution to be Maxwellian

$$f_0 = n \left( \frac{m}{2kT\pi} \right)^{3/2} e^{-\varepsilon/kT}$$

$$\text{Therefore } \frac{\partial f_0}{\partial \varepsilon} = -\frac{n}{kT} \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\varepsilon/kT} = -\frac{f_0}{kT} \quad \dots(13.23)$$

$$\text{Hence } j = \frac{\tau e^2 E}{kT} \int v_z^2 f_0 d^3 v \quad \dots(13.24)$$

$$\text{Since } \frac{1}{2} m \int v_z^2 f_0 d^3 v = \frac{1}{2} n k T \quad \dots(13.25)$$

$$\text{We have } j = \frac{n \tau e^2 E}{m} \quad \dots(13.26)$$

and the electrical conductivity

$$\sigma = \frac{n\tau e^2}{m} \quad \dots(13.27)$$

[compare with Eq. (12.36)]

### 13.5 A RIGOROUS FORMULATION OF THE TRANSPORT THEORY

In what follows, we will take  $r$  as a position vector and  $v$  as a velocity vector. We discussed above Boltzmann kinetic equation in the relaxation time approximation without taking into account the effects of interaction of the particles in equilibrium. We will now present a more rigorous formulation of the theory. We assume that the gas is so dilute that only binary collisions need be taken into account.

Consider a small volume element  $d^3r$ , located between  $r$  and  $r + dr$ . If collisions take place, molecules originally with positions and velocities not in the range  $d^3r$ ,  $d^3v$ , can be scattered into it and those originally in this range, can be scattered out.

The net increase in the number of molecules per unit time is  $\left(\frac{\partial f}{\partial t}\right)_{coll}$

$d^3r d^3v$ . Let  $D_c^{(-)} fd^3 rd^3 v$  denote the decrease and  $D_c^{(+)} fd^3 rd^3 v$  denote the increase in the number of molecules in unit time, where  $f$  is the distribution function.

$$\text{Therefore, } \left(\frac{\partial f}{\partial t}\right)_{coll} d^3 rd^3 v = D_c^{(+)} fd^3 rd^3 v - D_c^{(-)} fd^3 rd^3 v \quad \dots(13.28)$$

Let us now obtain the expressions for

$$D_c^{(-)} fd^3 rd^3 v \text{ and } D_c^{(+)} fd^3 rd^3 v$$

We have shown in Sec. 12.2 that the number of molecules scattered out of the volume element  $d^3r$ , due to collisions, per unit time is

$$(n_1 \langle V \rangle \sigma)(nd^3r) \quad \dots(13.29)$$

where  $n$  is the number of molecules per unit volume,  $n_1$  the number of molecules of the type whose scattering we are considering per unit volume;  $V$  the relative velocity and  $\sigma$  the scattering cross-section. In the present case suppose that the molecules  $A_2$  with velocity  $v_2$  collide with molecule  $A_1$ , with velocity  $V_1$ . From Eq. (13.29), the number of molecules  $A_2$  having velocities  $V_2$  and  $V_2 + dV_2$  and scattered out of the volume element  $d^3r$  is

$$[f_1(r, v_2, t) d^3 v_2 | v_1 - v_2 | \sigma(\Omega) d\Omega] f(r_1, v_1, t) d^3 v_1 d^3 r_1 \quad \dots(13.30)$$

The total number of molecules of the type  $A_2$  scattered by molecules  $A_1$ , per unit volume, can be found by integration over  $V_2$  and  $\Omega$ . Thus

$$D_c^{(-)} f = f(r, v_1 t) d^3 v_1 \int d^3 v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| f(r, v_2, t) \quad \dots(13.31)$$

After the collisions, the velocities of the molecules change to say  $V'_1$ , and  $V'_2$ .

For the calculation of  $D_c^{(+)} f$  we have to consider how many molecules end up after collision with a velocity in the range  $V_2$  and  $V_2 + dV_2$ , i.e. we have to consider inverse collisions. We, therefore, consider a beam of molecules with velocities  $V'_2$  incident upon molecules with velocities  $V'_1$ .

$$\text{Therefore } D_c^{(+)} = \int d^3 v'_2 \int \sigma'(\Omega) d\Omega |v'_1 - v'_2| f(r, v'_2, f) f(r, v'_1, t) d^3 v_1 \quad \dots(13.32)$$

In classical physics, inverse collision between two microscopic objects may be different from the original collision. This, however, is not true in the case of molecular collisions. A proper quantum mechanical calculation for small molecules shows that the cross-section for inverse encounter is the same as that for the original encounter i.e.

$$\sigma(v_1, v_2) |v'_1 v'_2| = \sigma(v'_1, v'_2 | v_1 v_2) \quad \dots(13.33)$$

or  $\sigma(\Omega) = \sigma'(\Omega)$

Since the collisions are assumed to be elastic, from the principle of conservation of energy

$$V = |v_1 - v_2| = |v'_1 v'_2| \quad \dots(13.34)$$

and, in accordance with the Liouville's theorem

$$d^3 v_1 d^3 v_2 = d^3 v'_1 d^3 v'_2 \quad \dots(13.35)$$

$$\begin{aligned} \text{Hence } & \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = D_c^{(+)} f - D_c^{(-)} f \\ & = \int d^3 v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| \{f(r, v'_1, t)f(r, v'_2, t) - f(r, v_1, t)f(r, v_2, t)\} \end{aligned}$$

or using the abbreviations

$$f_1 = f(r, v_1, t); f_2 = f(r, v_2, t); f'_1 = f(r, v'_1, t); f'_2 = f(r, v'_2, t)$$

$$\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = \int d^3 v_2 \int \sigma(\Omega) |v_1 - v_2| (f'_1 f'_2 - f_1 f_2) \quad \dots(13.36)$$

Hence, the Boltzmann non-linear integra-differential equation is

$$\begin{aligned} & \left( \frac{\partial f}{\partial t} \right) + v_1 \cdot \text{grad}_r f + \alpha \cdot \text{grad}_v f \\ & = \int v_2 \int_{\Omega} (f'_1 f'_2 - f_1 f_2) |v_1 - v_2| \sigma(\Omega) d\Omega d^3 v_2 \quad \dots(13.37) \end{aligned}$$

### 13.6 BOLTZMANN'S THEOREM

Boltzmann's integro-differential equation (13.37) is a general equation which describes the transport processes. How can we derive equilibrium distribution function from it? In the absence of external forces, the equilibrium distribution function is a solution of Eq. (13.37), for which  $f$  is independent of  $r$  and  $t$ . Therefore

$$\frac{\partial f}{\partial t} = 0, \quad \frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = \frac{\partial f}{\partial z} = 0 \text{ and } a = \frac{F}{m} = 0$$

Hence, the equilibrium solution, denoted by  $f_0(v)$  satisfies the equation

$$\left\{ \frac{\partial}{\partial t} + v \cdot \mathbf{grad}_r + \mathbf{a} \cdot \mathbf{grad}_v \right\} f_0(v) = 0 \quad \dots(13.38)$$

$$\text{or } \int_{v_2} \int_{\Omega} [f_0(v'_1)f_0(v'_2) - f_0(v_1)f_0(v_2)] |v_1 - v_2| \sigma(\Omega) d\Omega dv_2 = 0 \quad \dots(13.39)$$

We see that if

$$f_0(v'_1)f_0(v'_2) - f_0(v_1)f_0(v_2) = 0 \quad \dots(13.40)$$

$f_0(v)$  is a solution of Eq. (13.39). Eq. (13.40), therefore, is a sufficient condition for  $f(v)$  to be the solution of Eq. (13.39). We now show that this condition is also a necessary condition.

Let us examine, as was done by Boltzmann, the average properties of a quantity  $H(t)$  defined by

$$H(t) = \int d^3v f(v,t) \ln f(v,t) \quad \dots(13.41)$$

where  $f(v, t)$  is the distribution function.

$$\begin{aligned} \text{Therefore, } \frac{dH(t)}{dt} &= \int d^3v \left\{ \frac{\partial f}{\partial t} \ln f + f \frac{\partial \ln f}{\partial t} \right\} \\ &= \int d^3v (1 + \ln f) \frac{\partial f}{\partial t} \end{aligned} \quad \dots(13.42)$$

Therefore, for  $\frac{\partial f}{\partial t}$  to be zero,  $dH/dt$  has to be equal to zero.

$$\text{Hence } \frac{dH}{dt} = 0 \quad \dots(13.43)$$

is a necessary condition for  $\frac{\partial f}{\partial t}$  to be zero, that is, for  $f$  to be a solution of Eq. (13.39).

If  $f(v, t)$  satisfies the Boltzmann transport equation

$$\frac{\partial f(v,t)}{\partial t} = \int d^3v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| (f'_1 f'_2 - f_1 f_2) \quad \dots(13.44)$$

Substituting this in Eq. (13.42)

$$\frac{dH}{dt} = \int d^3v_1 \int d^3v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| (f'_1 f'_2 - f_1 f_2) (1 + \ln f_1) \dots (13.45)$$

Since  $\Omega$  = the angles between  $v_1 - v_2$  and  $v'_2 - v'_1$ ,  $\sigma(\Omega)$  is invariant under the following interchanges

$$(i) \quad v_1 \rightleftharpoons v_2 ; \quad v'_1 \rightleftharpoons v'_2$$

$$(ii) \quad v_1 \rightleftharpoons v'_1 ; \quad v_2 \rightleftharpoons v'$$

$$(iii) \quad v_1 \rightleftharpoons v'_2 ; \quad v_2 \rightleftharpoons v'_1$$

Therefore, interchanging  $v_1$  and  $v_2$ ;  $v'_1$  and  $v'_2$ , Eq. (13.45) changes to

$$\frac{dH}{dt} = \int d^3v_2 \int d^3v_1 \int \sigma(\Omega) |v_1 - v_2| (f'_2 f'_1 - f_2 f_1) (1 + \ln f_2) \dots (13.46)$$

Interchanging  $v_1$  and  $v'_1$ ;  $v_2$  and  $v'_2$

$$\frac{dH}{dt} = \int d^3v'_1 \int d^3v'_2 \int \sigma(\Omega) d\Omega |v'_2 - v'_1| (f_1 f_2 - f'_1 f'_2) (1 + \ln f'_1) \dots (13.47)$$

Interchanging  $v_1$  and  $v'_2$ ;  $v_2$  and  $v'_1$

$$\frac{dH}{dt} = \int d^3v'_2 \int d^3v'_1 \int \sigma(\Omega) d\Omega |v'_1 - v'_2| (f_2 f_1 - f'_2 f'_1) (1 + \ln f'_2) \dots (13.48)$$

We recall that  $d^3v_1 d^3v_2 = d^3v'_1 d^3v'_2$  and  $|v'_1 - v'_2| = |v_1 - v_2|$

Therefore, adding Eqs. (13.45), (13.46), (13.47) and (13.48) and dividing by 4, we get

$$\frac{dH}{dt} = \frac{1}{4} \int d^3v_1 \int d^3v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| (f'_1 f'_2 - f_1 f_2) \{ \ln(f_1 f_2) - \ln(f'_1 f'_2) \} \dots (13.49)$$

Since the integrand can never be positive for any set of  $f$ 's, the integral is either negative or zero. That is

$$\frac{dH}{dt} \leq 0 \dots (13.50)$$

$H$ , therefore, can never increase. This is known as *Boltzmann's H theorem*:  $H$ , thus, measures the deviation from the equilibrium state and has a tendency to decrease as a system approaches equilibrium.

One can easily see from, (13.49) that  $(dH/dt) = 0$  if and only if  $f'_1 f'_2 - f_1 f_2 = 0$ . Therefore

$$f'_1 f'_2 - f_1 f_2 = 0$$

is a necessary condition for  $f$  to be a solution of Eq. (13.39).

### 13.7 MAXWELL-BOLTZMANN DISTRIBUTION FROM BOLTZMANN'S EQUATION

We have seen that for  $f$  to be a solution of Boltzmann's equation (13.39), it is necessary that

$$f'_1 f'_2 - f_1 f'_2 = 0$$

Therefore  $\ln f'_1 + \ln f'_2 = \ln f_1 + \ln f_2$  ... (13.51)

This has the form of a law of conservation.

Let  $\ln f = \chi(v)$  ... (13.52)

Normally  $\chi(v)$  is a function of conserved quantities such as energy and momentum.

Therefore, let  $\chi(v) = -Av^2 + Bv + C'$  ... (13.53)

where  $A, B, C'$  are constants. With a proper choice of  $B$  and  $C'$ , Eq. (13.53) can be written as

$$\chi(v) = -A(v - v_0)^2 + \ln C \quad \dots(13.54)$$

Therefore  $\ln f = -A(v - v_0)^2 + \ln C$

or  $f = C e^{-A(v - v_0)^2}$  ... (13.55)

We now show that  $C$  and  $A$  have the same values as in MB distribution.

Density  $n$  is given by

$$n = \int f(r, v, t) d^3 v \quad \dots(13.56)$$

Therefore  $n = C \int f e^{-A(v-v_0)^2} d^3 v$

Putting  $v = v_0 + V$

$$n = C \int e^{-AV^2} d^3 V = C \left( \frac{\pi}{A} \right)^{3/2} \quad \dots(13.57)$$

Therefore  $C = n \left( \frac{A}{\pi} \right)^{2/3} \quad \dots(13.58)$

Now  $\langle v \rangle = \frac{\int v f(v) d^3 v}{\int f(v) d^3 v} = \frac{C}{n} \int v e^{-A(v-v_0)^2} d^3 v$

Since  $V = v - v_0$

$$\begin{aligned} \langle v \rangle &= \frac{C}{n} \int_{-\infty}^{\infty} (V + v_0) e^{-AV^2} d^3 V \\ &= \frac{C}{n} \int V e^{-AV^2} d^3 V + \frac{C}{n} v_0 \int e^{-AV^2} d^3 V \\ &= 0 + \frac{C}{n} v_0 \int e^{-AV^2} d^3 V \end{aligned}$$

$$= n \left( \frac{A}{\pi} \right)^{3/2} \frac{1}{n} \cdot v_0 \left( \frac{\pi}{A} \right)^{3/2} = v_0 \quad \dots(13.59)$$

If the gas as a whole does not have translational motion

$$\langle v \rangle = \langle v_0 \rangle = 0 \quad \dots(13.60)$$

Let us now find the value of the average energy

$$\langle \epsilon \rangle = \frac{\int \frac{1}{2} mv^2 f(v) d^3v}{\int f(v) d^3v} = \frac{mC}{2n} \int V^2 e^{-AV^2} d^3V \quad (\text{because } \langle v_1 \rangle = 0)$$

Using spherical polar coordinates

$$\begin{aligned} \langle \epsilon \rangle &= \frac{mC}{2n} \int V^4 e^{-AV^2} dV \sin\theta d\theta d\phi \\ &= \frac{2\pi mC}{n} \int_0^\infty V^4 e^{-Av^2} dV = \frac{2\pi mC}{n} \cdot \frac{3}{8} \cdot A^{-5/2} \sqrt{\pi} \\ &= \frac{2\pi mC}{n} n \left( \frac{A}{\pi} \right)^{3/2} \frac{3}{8} A^{-5/2} \sqrt{\pi} = \frac{3m}{4A} \end{aligned} \quad \dots(13.61)$$

$$\text{Therefore } A = \frac{3m}{4\langle \epsilon \rangle} = \frac{3m}{4 \cdot \frac{3}{2} kT} = \frac{m}{2kT} \quad \dots(13.62)$$

$$\text{and } C = n \left( \frac{A}{\pi} \right)^{3/2} = n \left( \frac{m}{2\pi kT} \right)^{3/2} \quad \dots(13.63)$$

$$\text{Hence } f_0(v) = n \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT}v^2} \quad \dots(13.64)$$

which is the MB distribution function.

### 13.8 H THEOREM IN QUANTUM MECHANICS

Let the Hamiltonian of a system be given by

$$H = H_1 + H' \quad \dots(13.65)$$

where  $H'$  is a contribution due to small interaction.

If the system is in a state  $r$ , the probability of its transition to a state  $s$  due to the interaction  $H'$  is

$$\omega_{rs} = \langle s | H' | r \rangle^2 = \langle s | H' | r \rangle^* \langle r | H' | s \rangle \quad \dots(13.66)$$

The probability for inverse transition

$$\omega_{sr} = \langle r | H' | s \rangle^2 = \langle r | H' | s \rangle^* \langle s | H' | r \rangle \quad \dots(13.67)$$

By the Hermitian property of the matrix elements

$$\langle s | H' | r \rangle^* = \langle r | H' | s \rangle \quad \dots(13.68)$$

Hence  $\omega_{rs} = \omega_{sr}$  ... (13.69)

This is the *principle of detailed balance*. The transition probability for a process and its inverse are equal.

Let  $P_r$  be the probability that a system is in a state  $r$ .

Therefore  $P_r = \frac{N_r}{N}$  ... (13.70)

where  $N_r$  is the number of systems in the state  $r$  and  $N$  the total number of systems.

Similarly  $P_s = \frac{N_s}{N}$  ... (13.71)

Now, there will be an increase in  $N_r$  with time as some systems make transition to  $r$  and also a decrease as some system may leave  $r$ . The net increase is given by

$$\frac{dN_r}{dt} = \sum_s N_s \omega_{sr} - \sum_s N_r \omega_{rs} \quad \dots(13.72)$$

Equation (13.72) is known as the *Master equation*.

Substituting for  $N_r$  and  $N_s$  from Eqs. (13.70) and (13.71), we have

$$\frac{dP_r}{dt} = \sum_s \omega_{rs} (P_s - P_r) \quad \dots(13.73)$$

Let  $h$  be the mean value of  $\ln P_r$  over all accessible states, i.e.

$$h = (\ln P_r) = \sum_r P_r \ln P_r \quad \dots(13.74)$$

(compare this definition of  $h$  with Eq. (13.41))

Therefore 
$$\begin{aligned} \frac{dh}{dt} &= \sum_r \left( \frac{dP_r}{dt} \ln P_r + \frac{dP_r}{dt} \right) \\ &= \sum_r \frac{dP_r}{dt} (\ln P_r + 1) \\ &= \sum_s \sum_r \omega_{rs} (P_s - P_r) (\ln P_r + 1) \end{aligned} \quad \dots(13.75)$$

Interchanging  $r$  and  $s$  does not affect the sum.

Therefore 
$$\frac{dh}{dt} = \sum_s \sum_r \omega_{rs} (P_r - P_s) (\ln P_s + 1) \quad \dots(13.76)$$

Adding and dividing by 2

$$\frac{dh}{dt} = -\frac{1}{2} \sum_s \sum_r \omega_{rs} (P_r - P_s) (\ln P_r - \ln P_s) \quad \dots(13.77)$$

Since  $(P_r - P_s) (\ln P_r - \ln P_s) \geq 0$  each term in the sum is positive and hence

$$\frac{dh}{dt} \leq 0 \quad \dots(13.78)$$

which proves the Boltzmann's theorem.

In Ch. 6 we have seen that

$$\frac{S}{k} = - \sum P_r \ln P \quad \dots(13.79)$$

Therefore  $\frac{S}{k} = -h$  ...(13.80)

This gives the relation between  $h$  and the entropy  $S$ .

This while  $h$  decreases with time, the entropy  $S$  increases with time, which is consistent with our earlier deduction.

It must be emphasized that

(a)  $\frac{dh}{dt} \leq 0$  i.e.,  $H$  Theorem is valid only if the gas satisfies the assumption is molecular chaos and

(b)  $\frac{dh}{dt} = 0$  if and only if  $f(v, t)$  is the MB distribution function.

### 13.9 VARIATION OF MEAN VALUES

We show in this section how the mean value of a quantity associated with a molecule varies as a function of  $t$  and  $r$ .

Let  $\chi(r, v, t)$  be a function which describes a property of a molecule of velocity  $v$  and located at  $r$  at time  $t$ . If  $n(r, t)$  is the mean number of molecules per unit volume and  $f(r, v, t)$  is the distribution function.

$$\langle \chi(r, t) \rangle = \frac{1}{n(r, t)} \int f(r, v, t) \chi(r, v, t) d^3 v \quad \dots(13.81)$$

Multiplying both sides of the Boltzmann's transport equation (13.37) by  $\chi_1 = \chi(r, v, t)$  and integrating over all velocities  $v_1$  we get

$$\begin{aligned} & \int \left( \frac{\partial}{\partial t} + v_1 \cdot \mathbf{grad}_r + \mathbf{a} \cdot \mathbf{grad}_v \right) f \chi_1 d^3 v_1 \\ &= \int d^3 v_1 \int d^3 v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| (f'_1 f'_2 - f_1 f_2) \chi_1 \end{aligned} \quad \dots(13.82)$$

LHS of this equation is

$$\begin{aligned} & \int \left( \frac{\partial}{\partial t} + v_1 \cdot \mathbf{grad}_r + \frac{F}{m} \mathbf{grad}_v \right) f \chi_1 d^3 v_1 \\ &= \int \frac{\partial f}{\partial t} \chi_1 d^3 v_1 + \int (v_1 \cdot \mathbf{grad}_r f) \chi_1 d^3 v_1 \times \\ & \quad \int \left( \frac{E}{m} \cdot \mathbf{grad}_v f \right) \chi_1 d^3 v_1 + \int f \frac{\partial \chi_1}{\partial t} d^3 v_1 \quad \dots(13.83) \end{aligned}$$

Now

$$(a) \quad \int \frac{\partial f}{\partial t} \chi_1 d^3 v_1 = \int \left\{ \frac{\partial}{\partial t} (f \chi_1) - f \frac{\partial \chi_1}{\partial t} \right\} d^3 v_1 \\ = \frac{\partial}{\partial t} \int f \chi_1 d^3 v_1 - \int f \frac{\partial \chi_1}{\partial t} d^3 v_1 \quad \dots(13.84)$$

Using Eq. (13.81)

$$\int \frac{\partial f}{\partial t} \chi_1 d^3 v_1 = \frac{\partial}{\partial t} (n \langle \chi_1 \rangle) - n \left\langle \frac{\partial \chi_1}{\partial t} \right\rangle \quad \dots(13.85)$$

$$(b) \quad \int (v_1 \cdot \text{grad}_r f) \chi_1 d^3 v_1 \\ = \int v_{1\alpha} \frac{\partial f}{\partial x_\alpha} \chi_1 d^3 v_1 \quad \dots(13.86)$$

In writing this, we have expressed vector quantities in terms of their Cartesian components and used summation convention.

Therefore

$$\int (v_1 \text{grad}_r f) \chi_1 d^3 v_1$$

$$= \int \left\{ \frac{\partial f}{\partial x_\alpha} (v_{1\alpha} f \chi_1) - v_{1\alpha} f \frac{\partial \chi_1}{\partial x_\alpha} \right\} d^3 v_1 \\ = \frac{\partial}{\partial \chi_a} (n \langle v_{1\alpha} \chi_1 \rangle) - n \langle v_{1\alpha} \frac{\partial \chi_1}{\partial x_\alpha} \rangle \quad \dots(13.87)$$

$$(c) \quad \int \left( \frac{F}{m} \cdot \text{grad}_v f \right) \chi_1 d^3 v_1 \\ = \int \frac{F\alpha}{m} \cdot \frac{\partial f}{\partial v_{1\alpha}} \chi_1 d^3 v_1 \\ = \int \left\{ \frac{\partial f}{\partial v_{1\alpha}} \cdot \left( \frac{F\alpha}{m} f \chi_1 \right) - \frac{F\alpha}{m} f \frac{\partial \chi_1}{\partial v_{1\alpha}} \right\} d^3 v_1 \\ = \left[ \frac{F\hat{\alpha}}{m} f \chi_1 \right]_{v_{1\alpha}=-\infty}^{v_{1\alpha}=+\infty} - \int \frac{F\hat{\alpha}}{m} f \frac{\partial \chi_1}{\partial v_{1\alpha}} d^3 v_1 \quad \dots(13.88)$$

Since  $f \rightarrow 0$  as  $v \rightarrow \infty$ , the first term vanishes. Hence

$$\int \left( \frac{F}{m} \cdot \text{grad}_v f \right) \chi_1 d^3 v_1 = \frac{F_a}{m} \left( n \left\langle \frac{\partial \chi_1}{\partial v_{1\alpha}} \right\rangle \right) \quad \dots(13.89)$$

Therefore, the L.H.S.

$$= \frac{\partial}{\partial t} (n \langle \chi_1 \rangle) - n \left\langle \frac{\partial \chi_1}{\partial t} \right\rangle + \frac{\partial}{\partial \chi_a} (n \langle v_{1\alpha} \chi_1 \rangle) - n \left\langle v_{1\alpha} \frac{\partial \chi_1}{\partial x_\alpha} \right\rangle \\ - \frac{F_a}{m} \left( n \left\langle \frac{\partial \chi_1}{\partial v_{1\alpha}} \right\rangle \right)$$

$$= \frac{\partial}{\partial t} (n \langle \chi_1 \rangle) + \frac{\partial}{\partial \chi_\alpha} (n \langle v_{1\alpha} \chi_1 \rangle) - n \left( \left\langle \frac{\partial}{\partial t} + v_{1\alpha} \frac{\partial}{\partial \chi_\alpha} + \frac{F_\alpha}{m} \frac{\partial}{\partial v_{1\alpha}} \right\rangle \chi_1 \right) \quad \dots(13.90)$$

Now, RHS  $\int d^3 v_1 \int d^3 v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| (f'_1 f'_2 - f_1 f_2) \chi_1 \quad \dots(13.91)$

Following the procedure adopted in the case of H-theorem, we make the following interchanges which leave  $\sigma(\Omega)$  unaffected:

$$(i) \quad v_1 \iff v_2; \quad v'_1 \iff v'_2$$

$$\text{RHS} = \int d^3 v_2 \int d^3 v_1 \int \sigma(\Omega) d\Omega |v_1 - v_2| (f'_2 f'_1 - f_2 f_1) \chi_2 \quad \dots(13.92)$$

$$\text{where } \chi_2 = \chi(r, v_2, t)$$

$$(ii) \quad v_1 \iff v'_1; \quad v_2 \iff v'_2$$

$$\text{RHS} = \int d^3 v'_1 \int d^3 v'_2 \int \sigma(\Omega) d\Omega |v'_1 - v'_2| (f_1 f_2 - f'_1 f'_2) \chi_1 \quad \dots(13.93)$$

$$(iii) \quad v_1 \iff v'_2; \quad v_2 \iff v'_1$$

$$\text{RHS} = \int d^3 v'_2 \int d^3 v'_1 \int \sigma(\Omega) d\Omega |v'_2 - v'_1| (f_2 f_1 - f'_2 f'_1) \chi'_2 \quad \dots(13.94)$$

Adding and dividing by 4

$$\text{RHS} = \frac{1}{4} \int d^3 v_1 \int d^3 v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| \times (f'_2 f'_1 - f_2 f_1) (\chi_1 + \chi_2 - \chi'_1 \chi'_2) \quad \dots(13.95)$$

Hence, Eq. (13.82) becomes

$$\begin{aligned} \frac{\partial}{\partial t} (n \langle \chi_1 \rangle) &= n \left\langle \left\{ \frac{\partial}{\partial t} + v_{1\alpha} \frac{\partial}{\partial \chi_\alpha} + \frac{F_\alpha}{m} \frac{\partial}{\partial v_{1\alpha}} \right\} \chi_1 \right\rangle \\ &- \frac{\partial}{\partial \chi_\alpha} (n \langle v_{1\alpha} \chi_1 \rangle) + \frac{1}{4} \int d^3 v_1 \int d^3 v_2 \int \sigma(\Omega) d\Omega |v_1 - v_2| \\ &\times (f'_1 f'_2 - f_1 f_2) (\chi_1 + \chi_2 - \chi'_1 \chi'_2) \dots(13.96) \end{aligned}$$

### 13.10 THE LAWS OF CONSERVATION

If  $\chi$  in the above treatment represents a conserved property

$$\chi_1 + \chi_2 = \chi'_1 + \chi'_2 \quad \dots(13.97)$$

and, hence, Eq. (13.96) reduces to

$$\frac{\partial}{\partial t} (n \langle \chi_1 \rangle) = n \left\langle \left\{ \frac{\partial}{\partial t} + v_{1\alpha} \frac{\partial}{\partial \chi_\alpha} + \frac{F_\alpha}{m} \frac{\partial}{\partial v_{1\alpha}} \right\} \cdot \chi_1 \right\rangle - \frac{\partial}{\partial \chi_\alpha} (n \langle v_{1\alpha} \chi_1 \rangle) \quad \dots(13.98)$$

The quantities that are conserved in collisions of neutral molecules are mass, momentum and energy.

## (A) Conservation of mass

Put  $\chi_1 = m$  in Eq. (13.96) we have

$$\frac{\partial}{\partial t} (nm) = - \frac{\partial}{\partial \chi_\alpha} \langle v_{1\alpha} m \rangle \quad \dots(13.99)$$

Here we have used Einstein's summation convention which means the repeated index  $\alpha$  is summed from 1 to 3.

Since  $\rho = nm$ , Eq. (13.99) becomes

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \chi_\alpha} \langle \rho v_{1\alpha} \rangle = 0$$

$$\text{i.e. } \frac{\partial \rho}{\partial t} + \Delta \langle \rho v_1 \rangle = 0 \quad \dots(13.100)$$

This is the equation of continuity.

Similarly, we can derive the equations for momentum and energy conservation.

**PROBLEMS**

- 13.1** Show that the average kinetic energy of two colliding hard spheres is  $\frac{7}{2} kT$ , of which  $\frac{3}{2} kT$  is associated with the centre of mass and  $2kT$  with the relative motion.
- 13.2** Estimate the probability that at any instant of time, a 1 cc volume of a room of dimensions 4 m  $\times$  3 m  $\times$  3m at NTP becomes totally devoid of air because of statistical fluctuations.
- 13.3** Find the value of the Lorenz number  $\frac{K}{\sigma T}$ , assuming that the electrons obeys Maxwell-Boltzmann statistics.
- 13.4** Assuming that a gas which flows with a velocity gradient  $\beta$  along the  $x$ -axis obeys classical statistics, find its coefficient of viscosity.



# APPENDIX

## APPENDIX A

### THE METHOD OF LAGRANGIAN UNDETERMINED MULTIPLIERS

In statistical mechanics one often needs to determine the extremum (maximum or minimum) value of a function of several variables under the condition that there exists some constraints between the variables. This can be done by adopting the method suggested by Lagrange.

Suppose the function whose extreme value is to be obtained is

$$f(x_1, x_2, \dots, x_n) \quad \dots(A.1)$$

subject to the condition that

$$\phi(x_1, x_2, \dots, x_n) = 0 \quad \dots(A.2)$$

To have an extremum value the function has to satisfy the condition

$$df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \dots + \frac{\partial f}{\partial x_n} dx_n = 0 \quad \dots(A.3)$$

where the derivatives are to be evaluated at the extremum points.

Since Eq. (A.2) is always satisfied

$$d\phi = \frac{\partial \phi}{\partial x_1} dx_1 + \frac{\partial \phi}{\partial x_2} dx_2 + \dots + \frac{\partial \phi}{\partial x_n} dx_n = 0 \quad \dots(A.4)$$

We have to solve Eq. (A.3) subject to the condition (A.4). We now introduce a parameter  $\alpha$  whose value will be determined later. We multiply the restrictive condition (A.4) by  $\alpha$  and subtract the result from Eq. (A.3). We get

$$\left( \frac{\partial f}{\partial x_1} - \alpha \frac{\partial \phi}{\partial x_1} \right) dx_1 + \left( \frac{\partial f}{\partial x_2} - \alpha \frac{\partial \phi}{\partial x_2} \right) dx_2 + \dots + \left( \frac{\partial f}{\partial x_n} - \alpha \frac{\partial \phi}{\partial x_n} \right) dx_n = 0 \quad \dots(A.5)$$

The variables  $x_1, x_2, \dots, x_n$  are not all independent. They are connected by Eq. (A.2).

Any one of these variables, say  $x_1$  may therefore, be expressed in terms of all other variables which can be chosen independently without

any restriction. Since the parameter  $\alpha$  is arbitrary, we can choose it so as to eliminate the coefficient of  $dx_1$ , i.e. we put

$$\frac{\partial f}{\partial x_1} - \alpha \frac{\partial \phi}{\partial x_1} = 0 \quad \dots(A.6)$$

From Eq. (A.5) we see that the sum of all others terms is equal to zero. Since the differentials  $dx_2, dx_3, \dots, dx_n$  are all independent, each of the brackets in Eq. (A.5) must be equal to zero.

$$\text{Therefore } \frac{\partial t}{\partial x_i} - \alpha \frac{\partial \phi}{\partial x_i} = 0 \text{ for } i = 1, 2, \dots, n \quad \dots(A.7)$$

These equations give us the value of  $\alpha$  and enable us to find the required extremum.

For example, suppose we have to find the maximum value of  $f(x, y) = xy$  subject to the condition that  $x^2 + y^2 = 1$ .

For maximum

$$df = xdy + ydx = 0$$

$$\text{Also} \quad 2x \, dx + 2y \, dy = 0$$

Multiplying the second equation by  $\alpha$  and subtracting it from the first, we get

$$(y - 2\alpha x)dx + (x - 2\alpha y)dy = 0$$

We choose  $\alpha$  so as to eliminate the first bracket, i.e.

$$y - 2\alpha x = 0 \text{ or } \alpha = \frac{y}{2x}$$

$$\text{Therefore } x - 2 \text{ or } y = x - \frac{y^2}{x} = 0; \alpha x = \pm y$$

From the restrictive condition  $x^2 + y^2 = 1$  we have

$$2x^2 = 1 \text{ or } x = \frac{1}{\sqrt{2}} = \pm y$$

Therefore the maximum value of  $f(x, y)$  is  $\frac{1}{2}$ .

## APPENDIX B

### SOME USEFUL INTEGRALS

#### 1. Gamma function

$$\begin{aligned} \Gamma(n+1) &= \int_0^\infty e^{-x} x^n dx = n \int_0^\infty e^{-x} x^{n-1} dx \\ &= n\Gamma(n) = n! \text{ if } n \text{ is integral} \end{aligned}$$

$$\text{and} \quad \Gamma(n+1) = 1(n-1) \dots \frac{3}{2} \frac{1}{2} \Gamma\left(\frac{1}{2}\right)$$

$$= n(n-1)\dots \frac{3}{2} \frac{1}{2} \sqrt{\pi} \text{ if } n \text{ is half-integral.}$$

2.  $I_n = \int_0^\infty x^n e^{-\alpha x^2} dx$  where  $n$  is a positive integer.

Substituting  $y = \alpha x^2$

$$I_n = \frac{1}{2} \alpha^{-(n+1)/2} \int_0^\infty e^{-y} y^{\frac{n-1}{2}} dy = \frac{1}{2} \alpha^{\frac{-(n+1)}{2}} \Gamma\left(\frac{n+1}{2}\right)$$

with even  $n = 2m$

$$I_{2m} = \frac{(2m-1)!}{2^{m+1}} \sqrt{\frac{\pi}{\alpha^{2m+1}}}$$

and with odd  $n = 2m + 1$

$$I_{2m+1} = \frac{m!}{2\alpha^{m+1}}$$

The integral

$$\int_{-\infty}^{\infty} x^n e^{-\alpha x^2} dx = \begin{cases} 0 & \text{when } n \text{ is odd} \\ 2I_n & \text{when } n \text{ is even} \end{cases}$$

3. The error function

$$\begin{aligned} y &= \frac{2}{\sqrt{\pi}} \int_0^y e^{-x^2} dx \\ &= \frac{2}{\sqrt{\pi}} \left( y - \frac{y^3}{3} + \frac{y^5}{10} + \dots \right) \text{ if } y \ll 1 \\ \text{and} \quad &= 1 - \frac{e^{-y^2}}{y\sqrt{\pi}} \left( 1 - \frac{1}{2y^2} + \dots \right) \text{ if } y \gg 1 \end{aligned}$$

4.  $\int_{-\infty}^{\infty} \frac{x^2}{(e^x + 1)(e^{-x} + 1)} dx = \frac{\pi^2}{3}$

5.  $\int_0^{\infty} \frac{x^{n-1}}{e^x - 1} dx = \Gamma(n) \xi(n)$  for all  $n > 1$ , where  $\xi(n)$  is the Riemann Zeta function.

The numerical values of some of the  $\xi(n)$  are

$$(i) \quad \xi(2) = \frac{\pi^2}{6} \approx 1.645 \quad (ii) \quad \xi(3) \approx 1.202$$

$$(iii) \quad \xi(4) : \frac{\pi^2}{90} \approx 1.082 \quad (iv) \quad \xi(5) \approx 1.037$$

$$(v) \quad \xi\left(\frac{3}{2}\right) = 2.612 \quad (vi) \quad \xi\left(\frac{5}{2}\right) = 1.341$$

**APPENDIX C****1. PHYSICAL CONSTANTS**

<b>Constant</b>	<b>Value</b>
Speed of light $c$ (in vacuum)	$2.998 \times 10^8 \text{ ms}^{-1}$
Electronic charge $e$	$1.602 \times 10^{-19} \text{ coulombs}$
Electron rest mass $m_e$	$9.109 \times 10^{-31} \text{ kg}$
Proton rest mass $m_p$	$1.673 \times 10^{-27} \text{ kg}$
Planck's constant $h$	$6.626 \times 10^{-34} \text{ Js}$
Boltzmann constant $k$	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gravitational constant $G$	$6.67 \text{ Nm}^2 \text{ kg}^{-2}$
Bohr magneton $\mu_B$	$9.271 \times 10^{-24} \text{ J T}^{-1}$
Avogadro number $N_A$	$6.023 \times 10^{23} \text{ mole}^{-1}$
Molar gas constant $R$	$8.3144 \text{ J/mole}$
Molar volume at STP	$2.242 \text{ m}^3/\text{mole}$

**2. CONVERSION FACTORS**

1 Newton N	$10^5$ dynes
1 Joule (J)	$10^7$ ergs
1 Cal	4.19 J
1 Electron-volt (eV)	$\begin{cases} 1.062 \times 10^{-19} \text{ J} \\ 23.05 \text{ k cal/mole} \end{cases}$
1 Atmosphere	$1.01323 \times 10^5 \text{ N/m}^2 (P_0)$

**ANSWERS TO PROBLEMS****Chapter 2**

**2.1**  $dp = \frac{d\phi}{n\sqrt{\phi_0^2 - \phi^2}}$

**2.2**  $2 \times 10^{-8}$

**2.3**  $(0.8)^3 (0.9)^4 = 0.336$

**2.4** 31/32

**2.5** 0.65

**2.6** (a) 0.40, (b) 0.60, (c) 0.16

**2.7** (a) (i) 0.444; (ii) 0.444

(b) (i) 0.437, (ii) 0.46

**2.8** (i)  $\langle \mu \rangle = 0$  (ii)  $\langle \mu^2 \rangle = 2p \mu_0^2$ . (iii)  $\langle \Delta\mu^2 \rangle = 2p\mu_0^2$

**2.9** (a) 0.37 (b) 0.08

**2.10**  $0.8 \times 10^{-23}$

**Chapter 3**

**3.1**  $2.4 \times 10^{12}$   $3.4 \times 10^4$  K

**3.2**  $1.93 \times 10^3$  m/s

**Chapter 4**

**4.1** 3, 20

$$\mathbf{4.4} \quad p = \pm \sqrt{2mee_1 \left( \frac{1}{r} - \frac{1}{r_0} \right)}$$

**4.5** Elliplic helix  $\left( x^2 + \frac{p^2}{m^2\omega^2} \right)^{\frac{1}{2}} = \left( x_0^2 + \frac{p_0^2}{m^2\omega^2} \right) e^{-r\Gamma}$

**Chapter 5**

**5.1**  $kT$

**5.2** (i)  $p_1 = 0.8$ ,  $p_2 = 0.2$  T = 5.25 K      (ii)  $p_1 = p_2 = 0.5$ , T =  $\infty$

**5.4** (i)  $2.0 \times 10^{23}$ , (ii) 2.04 J

**5.5**  $kT$

**5.6**  $\frac{3}{2}kT$

**5.7**  $kT/mg$

**5.8** 40 km

**5.9**  $12 \times 10^{-6}$  m

**5.10** 304 K

**Chapter 6**

**6.1**  $P = NkT \frac{\beta m \omega^2}{2\pi l} \frac{e^{\beta m \omega^2 k^2}}{e^{\beta m \omega^2 R^2 / 2} - 1}$

**6.2** 147 J

**6.6** (i)  $S = 0$ ; (ii)  $S = pN \ln 2$

**6.7** (i)  $(1.554)^N$ ; (ii) 0.50 Ne; (iii) 0.94 Nk

**6.8** (i)  $NkT \ln \left( \frac{\hbar\omega}{kT} \right)$ ; (ii)  $Nk \left[ \ln \frac{kT}{\hbar\omega} + 1 \right]$  (iii)  $\mu = kT \ln \left( \frac{\hbar\omega}{kT} \right)$

**6.9** 124 JK<sup>-1</sup>

**6.10**  $-5.98 \times 10^{-20}$  J

**6.11** 3000 K

**6.14**  $Nk \ln \frac{(P_1 + P_2)^2}{4P_1 P_2}$

**6.15** 20.8 JK<sup>-1</sup>.

**Chapter 7**

**7.4**  $\frac{3}{2}kT$

**Chapter 8**

**8.2**  $\frac{\hbar\omega}{2} \left\{ 1 + 3e^{-\beta\hbar\omega} \right\} \left\{ 1 + e^{-\beta\hbar\omega} \right\}^{-1}$

**8.3** (i) valid; (ii) not valid

**8.4**  $4 \times 10^{-9}$

**8.6**  $\sum 3(2j+1)e^{-J(J+1)\theta/T}$

**8.7** 0.92 Nk

**8.8** 2452 K;

**8.10**  $2.7 \times 10^{-2}$  Pa

**Chapter 9**

**9.2**  $2.7 \text{ kT}; 9:3 \frac{e^{\beta\epsilon_s}}{(e^{\beta\epsilon_s-1})^2}$

**9.4** 218 hours

**9.5** (i)  $\sigma T_s^4 \left(\frac{R}{L}\right)^2$  (ii) 283 K

**9.7** 0.087 K;

**9.8** 0.91

**Chapter 10**

**10.1** (i)  $5 \times 10^{-19} \text{ J}$  (ii)  $0.47 \times 10^2 \text{ T}$

**10.2** 3/4

**10.3** 1567 Km/s

**10.6** 3

**10.7**  $2 \times 10^{10} \text{ Pa}$

**10.8**  $3 \times 56 \times 10^{-10}$

**10.9**  $C_v = \frac{(3\pi^2)^{2/3}}{3ch} \left(\frac{V}{n}\right)^{1/3} kT$

**10.10**  $\chi = 3 \left(\frac{N}{V}\right) \frac{\mu_m^2}{2\epsilon_F}$

**Chapter 11**

**11.1**  $V_c = 2 b; p_c = \frac{a}{4b^2c^2}; T_c = \frac{a}{4Rb}$

**11.2**  $2.3 \times 10^6 \text{ J/kg}$

**11.3**  $b = 2.2 \times 10^{-5} \text{ m}^3 \text{ mole}; a = 1.69 \times 10^{-2} \text{ Pa m}^6/\text{mole}$   
 $R = 6.86 \text{ J/mole K}$

**11.4** (i)  $P = 2.53 \times 10^6 \text{ Pa}; P_{ideal} = 2.49 \times 10^6 \text{ Pa}$   
(ii)  $P = 1.39 \times 10^6 \text{ Pa}; P_{ideal} = 2.91 \times 10^6 \text{ Pa}$

**11.5** -0.009 K

**Chapter 12**

**12.1**  $2 \times 10^{-4}$

**12.2**  $1 = \frac{e\varepsilon\tau^2}{m}$

**12.4** (i)  $1.7 \times 10^{-7} \text{ m}; (ii) 1.1 \times 10^{-10} \text{ m}$

**12.5**  $\frac{1}{4} c \frac{N}{V}$

**12.6**  $2kT$

**12.8**  $2.1 \times 10^{-3} \text{ torr}$

**12.12** ~3 hrs.

**Chapter 13**

**13.3**  $3 \left(\frac{k}{e}\right)^2$

**13.4**  $\eta = n kT \tau$



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