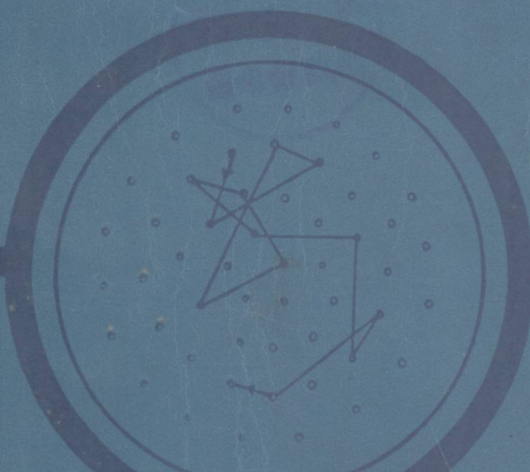
THERMODYNAMICS AND STATISTICAL PHYSICS

SHARMA • SARKAR



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THERMODYNAMICS AND STATISTICAL PHYSICS

[*For B.Sc., B.Sc. (Hon.) & B.E. Students of all Indian Universities*]

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Preface

The revolution in Physics, which started with the beginning of this century, can be attributed to the study of Thermodynamics and Statistical Physics. The failure of classical ideas in explaining the spectrum of blackbody radiation and specific heats of solids and gases were mainly responsible for the new ideas of Quantum Physics. Hence a deep understanding of principles of Thermodynamics and Statistical Physics is essential in order to appreciate the modern concepts in Physics.

The authors who have taught the subject to the undergraduate students for a decade have felt the student's difficulty in understanding basic concepts of thermodynamics like 'entropy'. Students at this level are not able to appreciate the beauty and power of statistical methods and this acts as a hinderance in their over-all understanding of Physics. Classics on the subject by Zemansky, Sears and Saha and Shrivastava act as excellent reference books for bright students but an average student finds them difficult to use. This book is an effort to present the concepts of Thermodynamics and Statistical Physics in such a manner as to be understable to average students of our universities and colleges. The noteworthy features of this book are :

(*a*) Fundamental concepts have been explained in a simple and clear manner without a compromise for their exactness.

(*b*) The language has been kept straight-forward and simple.

(*c*) Large number of solved numerical examples have been given which help the students to develop an understanding of the subject.

(*d*) Number of illustrations and tables have been used to supplement the text.

(*e*) Many questions and problems at the end of each of the chapters have been selected from examination questions of various Indian universities. This will help the students to prepare accordingly.

(*f*) The book covers the syllabus of most of the Indian universities. The chapter on Thermal Conduction has been included with this purpose although it does not directly form a part of 'Thermodynamics and Statistical Physics'.

(g) S.I. system of units and symbols has been used throughout the text although some problems are given in C.G.S. units as well.

The authors wish to express gratefulness to their colleagues who have given useful suggestions and discussed some parts of manuscript critically. They are also thankful to Mr. S.K. Joshi of M/S Himalaya Publishing House for his efforts in bringing out the book in present form. The services rendered by M/S U.P. printers are also thankfully acknowledged.

Suggestions and criticism for improvement of the book from fellow teachers and students who will be using this shall be gratefully acknowledged.

Agra

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Zeroth Law of Thermodynamics and Temperature

1.1. Fundamental Concepts and Nomenclature

Thermodynamics is one of the cardinal branches of Physics which is a perfect mathematical science describing the inter-relationship between heat and any diverse form of energy *viz.* mechanical, electrical, magnetic, chemical etc. The basic concept starts with the transformation of heat into mechanical work through any bulk matter. It has innumerable applications in Physics, Chemistry and Engineering Sciences.

It has become quite an established theory now that a bulk matter constitutes of molecules and atoms which themselves are made up of protons, neutrons, electrons etc. Atomic and Nuclear Physics are other two well developed branches of Physics which supply considerable knowledge about the interactions between these fundamental particles. The mathematics of such interactions makes it possible to analyse the properties of bulk matter like thermal expansion, elasticity, specific heat etc. in terms of the detailed structure of matter. However, the study of thermodynamics takes no account of the atomic constitution, though the atomic interactions, the interactions between electrons, protons, neutrons etc., are stronger than that between two or more molecules. This is because the descriptions of most of the bulk properties of matter do not need to consider the internal changes occurring within the molecules or atoms. Thus in order to understand the thermodynamical properties of bulk matter, the intermolecular interactions will be taken as sufficient. In the future text of the book, however, some special treatment may use the interactions between electrons, protons, neutrons etc.

For all practical purposes, now onward a bulk system will be thermodynamically called a *macroscopic system* while the molecules, which form a "*macro*" body will be called the *microscopic system.* The microscopic interactions will interpret the properties of macroscopic system. The validity of the names 'macro' and 'micro' is quite evident in the sense that the number of molecules in one gram mole of any substance is 6.06×10^{23} (Avogadro's number). This obviously indicates that 2 gm of hydrogen or 32 gm of oxygen have 6.06×10^{23} molecules. Volume-wise, even a gas at normal temperature and pressure, which has smallest number of molecules per unit volume as compared to liquids and solids, will have approximately 3×10^{25} molecules in one cubic metre (one gm mole of a gas occupy $2.2\times10^{-2}m^3$ at normal temperature and pressure). Such a huge number of molecules in a small volume or mass of gas proves the validity of terms '*micro*' and '*macro*' for molecules and total bulk respectively.

The internal changes occurring inside a molecule give rise to the *rotational*, *vibrational* and *electronic* energies in discrete steps. The state of a molecule with the lowest possible energy is called the *ground state* and with respect to the ground state, all other states are called *excited states*. These are the *internal energy states of a molecule*. However, molecules in a bulk matter will always have *potential and kinetic energies* due to intermolecular interactions and their own translational motions respectively. In a well defined coordinate frame of reference the position coordinate gives the potential energy and momenta coordinates give the kinetic energy. Since the position and momenta coordinates give the external description of the molecules, the potential and kinetic energies are called *external energies of molecules*. Our present context will not deal, in general, with the internal energy states of the molecules as the molecules themselves are defined as 'micro' system.

We describe the relative microscopic and macroscopic motions of a bulk matter of mass M in Fig. 1.1. Let us consider a frame of reference XYZ fixed in laboratory in which the mass M is moving with a uniform velocity $\vec{V}$. One can fix another frame of reference xyz with its origin at the centre of mass of that body and the velocities of the molecules inside the body may be referred to in this c.m. frame (c.m. stands for centre of mass).

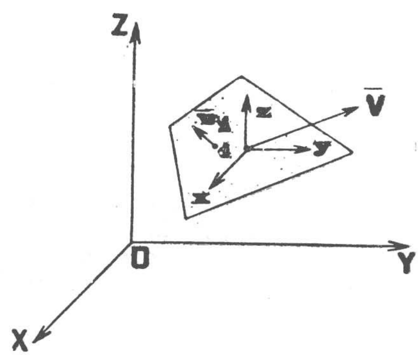

Fig. 1.1. Relative microscopic and microscopic movements.

Let $\vec{v_i}$ be the velocity of ith molecule in c.m. frame. C.m. frame itself has a relative velocity $\vec{V}$ with respect to lab frame (Lab stands for laboratory). Since the relative velocity of the entire body with respect to c.m. frame is zero, the total momentum is zero, *i.e.*,

$$\Sigma_i\, m_i \vec{v_i}=0 \qquad \ldots(1.1)$$