THERMAL PHYSICS

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PREFACE

This book, in its preliminary form, has been used as a text in the subject "Statistical Mechanics and Thermodynamics," a one-semester course required of seniors majoring in physics at the Massachusetts Institute of Technology and also taken by mathematics and electrical engineering majors. Prerequisites for the subject are introductory calculus, introductory mechanics, and a course in atomic physics that includes the ideas of quantization and atomic structure. The material in it and in two other senior subjects, classical mechanics and electromagnetic theory, are required of entering graduate students before they can progress to strictly graduate subjects in physics.

     The material in this revised and considerably expanded edition has been chosen to prepare the student to go on into fields of modern statistical physics, such as low-temperature physics, solid-state physics, and plasma physics. Thus the illustrative material includes discussions of the properties of liquid helium, super-conductors, and paramagnetic substances. To emphasize the fact that thermodynamics is more than a study of the relationships between pressure, volume, and temperature, the thermomagnetic properties of materials that obey Curie's law are discussed in some detail, instead of the usual examples taken from physical chemistry.

These illustrative topics are each taken up several times in the course of the text, to illustrate new concepts or techniques as they are encountered.

The text follows roughly the historical development of the subject, beginning with thermodynamics, going on to kinetic theory, and then to classical and quantum statistical mechanics. Emphasis is laid on the fact that the subject is still developing, is not yet in its final, moribund form. Mention is made of basic changes that have had to be made in the theory to accommodate new experimental data, and it is suggested that other changes may have to be made in the future. Thus the presentation carries forward the point of view enunciated in the Preface to the Physical Science Study Committee text, "that physics is a developing subject, and that this development is the imaginative work of men and women like the student himself".

The topics covered in the present expanded version are rather more than can be taught in one semester to the average physics major. To reduce the amount of assigned material, the latter portions of Chapters 7, 8, 13, 14, 15, 21, 22, 25, or 26 and all of Chapters 10 or 27, or both, may be omitted. In the one-semester subject given at M.I.T., illustrative material from four or five of these more specialized topics is discussed in the lectures, which are three hours per week, and one or two others are taken up in the problem sections, which are one hour per week. It has been found that the more advanced students will read, and absorb, most of the material in the present book.

The problems, listed at the ends of chapters, have been chosen to illuminate basic concepts rather than for drill in techniques. Usually only two or three such problems are assigned each week; these are discussed in some detail in the problem sections. At times the instructors have assigned or have discussed additional drill problems specifically written to improve the student's facility in handling some techniques.

Because the subject of thermal physics impinges on so many parts of physics, the duplication of symbolism is unavoidable if one tries to conform to standard notation in each of the fields touched on. Some ameliorization has been achieved by use of different type fonts, such as German script for magnetization, magnetic and electric intensity, etc. It is hoped that confusion will be minimized with the help of the Glossary of Terms, in which is listed the place or places in the text where the symbol is defined.

Since this is a text, not a treatise, no references are given to original papers on various subjects. The bibliography lists other texts which cover some aspect in more detail, or from a different point of view.

In developing the present volume the author has had valuable assistance from many of his colleagues, notably from Professors L. Tisza, F. Villars, and L. C. Bradley. They are to be thanked for numerous improvements and corrections; they should not be blamed for the shortcomings that remain.

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CHAPTER

INTRODUCTION

The subject matter of this book, thermodynamics, kinetic theory, and statistical mechanics, constitutes the portion of physics having to do with heat. Thus it may be called *thermal physics*. Since heat and other related properties, such as pressure and temperature, are characteristics of aggregates of matter, the subject constitutes a part of the physics of matter in bulk. Its theoretical models, devised to correspond with the observed behavior of matter in bulk (and to predict other unobserved behavior), rely on the mathematics of probability and statistics; thus the subject may alternatively be called *statistical physics*.

Historical

The part of the subject called thermodynamics has had a long and controversial history. It began at the start of the industrial revolution, when it became important to understand the relation between heat and chemical transformations and the conversion of heat into mechanical energy. At that time the atomic nature of matter was not yet understood and the mathematical model, developed to represent the relation between thermal and mechanical behavior, had to be put together with the guidance of the crude experiments that could then be made. Many initial mistakes were made and the theory had to be drastically revised several times. This theory, now called thermodynamics, concerns itself solely with the macroscopic properties of aggregated matter, such as temperature and pressure, and their interrelations, without reference to the underlying atomic structure. The general pattern of these

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interrelations is summarized in the laws of thermodynamics, from which one can predict the complete thermal behavior of any substance, given a relatively few empirical relationships, obtained ·by macroscopic measurements made on the substance in question.

In the latter half of the nineteenth century, when the atomic nature of matter began to be understood, efforts were made to learn how the macroscopic properties of matter, dealt with by thermodynamics, could depend on the assumed behavior of constituent atoms. The first successes of this work were concerned with gases, where the interactions between the atomic components are minimal. The results provide a means of expressing the pressure, temperature, and other macroscopic properties of the gas in terms of average values of properties of the molecules, such as their kinetic energy. This part of the subject came to be called *kinetic theory*.

In the meantime a much more ambitious effort was begun by Gibbs in this country, and by Boltzmann and others in Europe, to provide a statistical correspondence between the atomic substructure of any piece of matter and its macroscopic behavior. Gibbs called this theory *statistical mechanics*. Despite the fragmentary knowledge of atomic physics at the time, statistical mechanics was surprisingly successful from the first. Since then, of course, increased atomic knowledge has enabled us to clarify its basic principles and extend its techniques. It now provides us with a means of understanding the laws of thermodynamics and of predicting the various relations between thermodynamic variables, hitherto obtained empirically.

Thermodynamics and Statistical Mechanics

Thus thermodynamics and statistical mechanics are mutually complementary. For example, if the functional relationship between the pressure of a gas, its temperature, and the volume it occupies is known, and if the dependence of the heat capacity of the gas on its temperature and pressure has been determined, then thermodynamics can predict how the temperature and pressure are related when the gas is isolated thermally, or how much heat it will liberate when compressed at constant temperature. Statistical mechanics, on the other hand, seeks to derive the functional relation between pressure, volume, and temperature, and also the behavior of the heat capacity, in terms of the properties of the molecules that make up the gas.

In this volume we shall first take up thermodynamics, because it is more obviously related to the gross physical properties we wish

to study. But we shall continue to refer back to the underlying microstructure, by now well understood, to remind ourselves that the thermodynamic variables are just another manifestation of atomic behavior. In fact, because it does not make use of atomic concepts, thermodynamics is a rather abstract subject, employing sophisticated concepts, which have many logical interconnections; it is not easy to understand one part until one understands the whole. In such a case it is better pedagogy to depart from strict logical presentation. Hence several derivations and definitions will be given in steps, first presented in simple form and, only after other concepts have been introduced, later re-enunciated in final, accurate form.

Part of the difficulty comes from the fact, more apparent now than earlier, that the thermodynamic quantities such as temperature and pressure are aggregate effects of related atomic properties. In thermodynamics we assume, with considerable empirical justification, that whenever a given amount of gas, in a container of given volume, is brought to a given temperature, its pressure and other thermodynamic properties will take on specific values, no matter what has been done to the gas previously. By this we do not mean that when the gas is brought back to the same temperature each molecule of the gas returns to the same position and velocity it had previously. All we mean is that the average effects of all the atoms return to their original values, that even if a particular molecule does not return to its previous position or velocity, its place will have been taken by another, so that the aggregate effect is the same.

To thus assume that the state of a given collection of atoms can be at all adequately determined by specifying the values of a small number of macroscopic variables, such as temperature and pressure, would at first seem to be an unworkable oversimplification. Even if there were a large number of different configurations of atomic positions and motions which resulted in the same measurement of temperature, for example, there is no a priori reason that all, or even most, of these same configurations would produce the same pressure. What must happen (and what innumerable experiments show does happen) is that a large number of these configurations do produce the same pressure and that thermodynamics has a method of distinguishing this subset of configurations from others, which do not produce the same pressure. The distinguishing feature of the favored subset is embodied in the concept of the equilibrium state.

Equilibrium States

A detailed specification of the position, velocity, and quantum state of each atom in a given system is called a *microstate* of the system. The definition is useful conceptually, not experimentally, for we cannot determine by observation just what microstate a system is in at some instant, and we would not need to do so even if we could. As we said before, many different microstates will produce the same macroscopic effects; all we need to do is to find a method of confining our attention to that set of microstates which exhibits the simple relations between macroscopic variables, with which thermodynamics concerns itself.

Consider for a moment all those microstates of a particular gas for which the total kinetic energy of all the molecules is equal to some value U. Some of the microstates will correspond to the gas being in a state of turbulence, some parts of the gas having net momentum in one direction, some in another. But a very large number of microstates will correspond to a fairly uniform distribution of molecular kinetic energies and directions of motion, over all regions occupied by the gas. In these states, which we shall call the equilibrium microstates, we shall find that the temperature and pressure are fairly uniform throughout the gas. It is a fact, verified by many experiments, that if a gas is started in a microstate corresponding to turbulence, it will sooner or later reach one of the equilibrium microstates, in which temperature and pressure are uniform. From then on, although the system will change from microstate to microstate as the molecules move about and collide, it will confine itself to equilibrium microstates. To put it in other language, although the gas may start in a state of turbulence, if it is left alone long enough internal friction will bring it to that state of thermodynamic quiescence we call *equilibrium*, where it will remain.

Classical mechanics, as developed by Newton, Lagrange, and Hamilton, is able to predict the behavior of systems with a few elements, or with many elements arranged in some very symmetrical pattern. The two-body problem of celestial mechanics is not difficult to work out in complete detail, but the three-body problem has not yet been solved in general. The motions of many molecules can be worked out only if they are held in some regular pattern by elastic forces, as in a crystal; otherwise the solution is beyond our largest electronic computers. Thermodynamics, on the other hand, deals with the opposite kind of problem, with aggregates of molecules