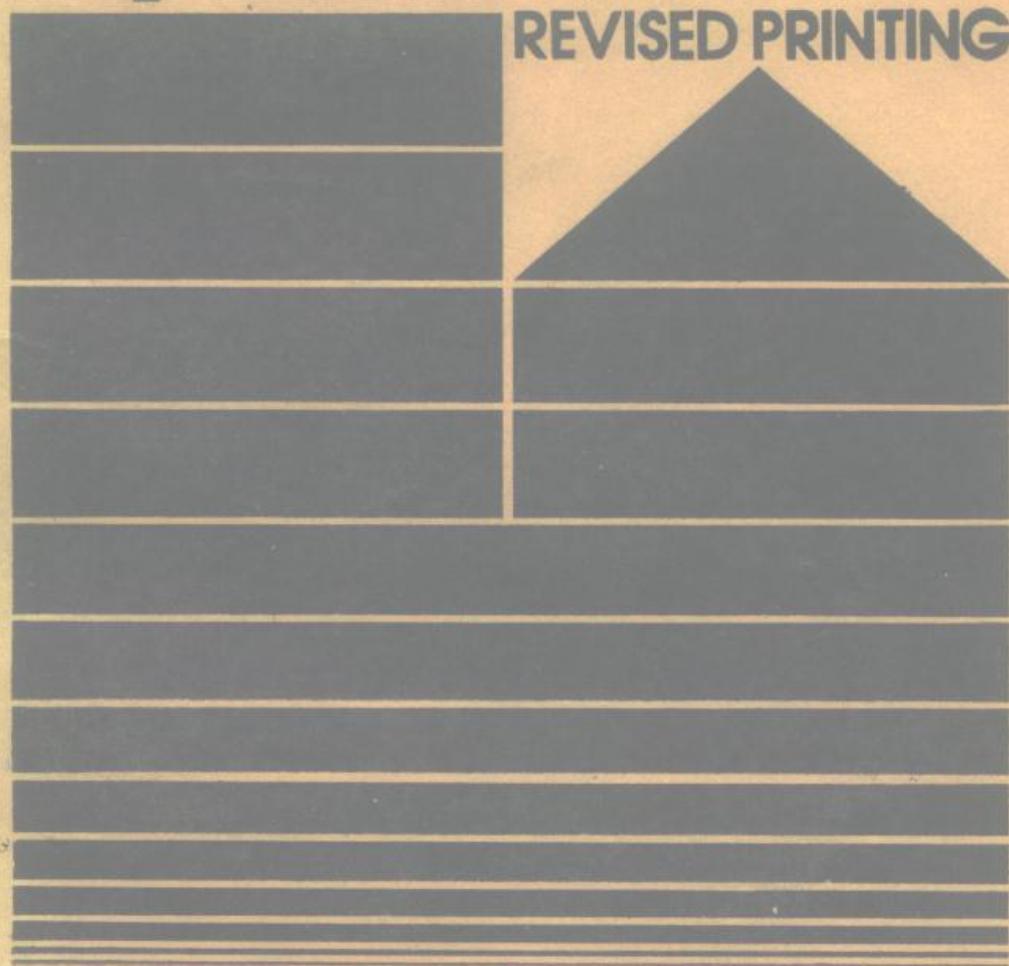


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CHANG L. TIEN
JOHN H. LIENHARD

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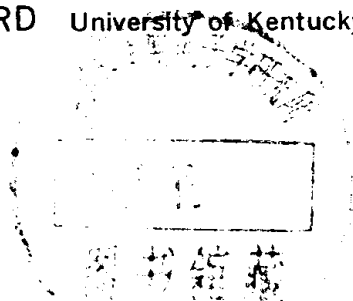
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Statistical Thermodynamics

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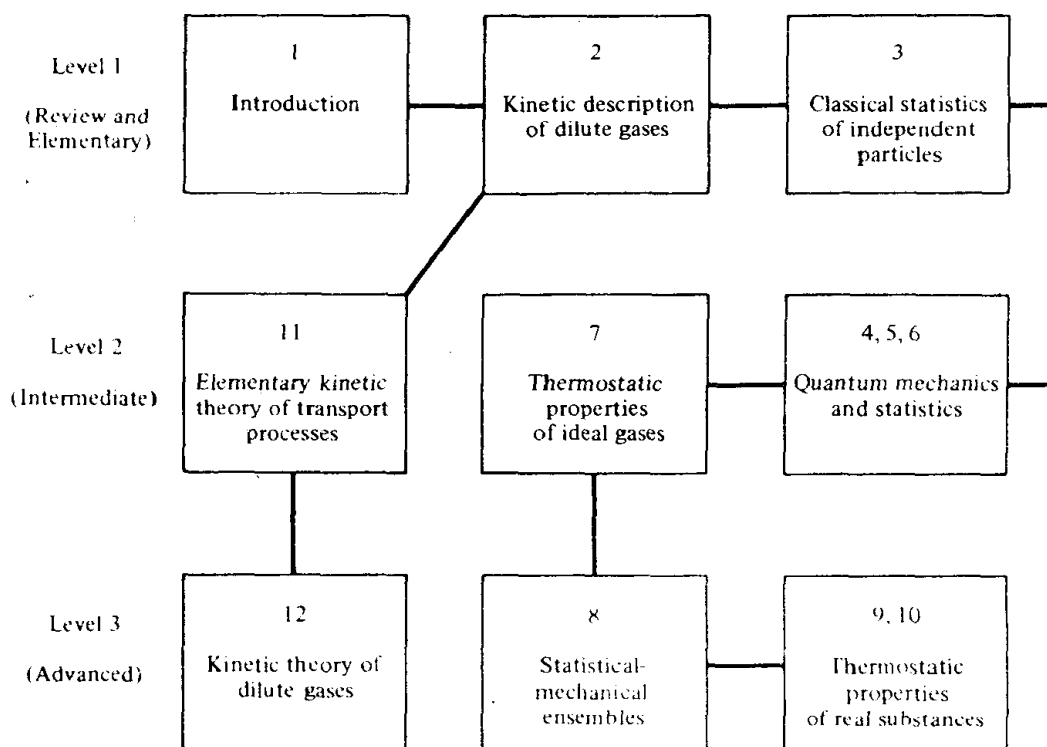
Preface

This book has been developed to meet the needs of advanced engineering undergraduate and beginning graduate students for an introduction to statistical thermodynamics. The student that we have envisioned has had at least an introductory course in thermodynamics; he may or may not have had a course in modern physics; and he has had no physics beyond that level. Nor do we presuppose a course in statistics or a mathematics background beyond that which he normally would have developed for his upper-division engineering work. Such a student, although he is capable of learning fairly rapidly, must start at the beginning level as far as the concepts of quantum mechanics and modern physics are concerned.

During the past seven years we first developed class notes, and subsequently organized them into the present text. This text has been developed in close conjunction with classes at the University of California at Berkeley, Washington State University at Pullman, and the University of Kentucky at Lexington.

What we have evolved is an approach that escalates the ped-

agogical level as it proceeds. The twelve chapters are arranged into a sequence of basic subject groups presented on three pedagogical levels as shown.



The first three chapters are intended to establish an elementary background, and a language, on which the material in the subsequent chapters is based. Our experience has shown that these should not be covered too rapidly. The fourth and fifth chapters largely contain the needed material that would have been covered in an elementary modern physics course. The detail in which they should be treated will vary according to the background of the class. Chapters 6 and most of 7 and 11 would complete an introduction to the methods of statistical thermodynamics. Depending upon the level of the students, a one-semester course can encompass some or all of the additional material and applications developed in Chapters 8, 9, 10, and 12.

The exposition of the subject is developed with the following objective in mind: We want to bring the student to an appreciation of the role of statistical-thermodynamics methods so that he will understand why they are important, what they can do, and how they can be applied to various engineering systems. Therefore, we have attempted to stay relatively close to the historical evolution of the subject and we have sought to carry this evolution to its fruition in

applications. In this connection we have also tried to keep the unity of the subject clear in the student's mind by showing respect for the axiomatic structure of the subject.

In establishing methods for computing the physical properties of substances in equilibrium, for example, we have made strong use of the notion of a *fundamental equation* or generating relation for physical properties. This idea is first developed in Chapter 1 from a strictly macroscopic viewpoint. In subsequent chapters we take care to show how the microscopic generating functions (partition function, q potential, grand canonical partition function, etc.) relate to the macroscopic ones (entropy, energy, the free energies, etc.).

We have attempted, wherever it is appropriate to do so, to demonstrate the usefulness and strength of statistical thermodynamics through simple applications that are important in modern engineering problems. Falling into this category are, for instance, the treatment of the Lighthill dissociating gas and the singly ionized gas, the emphasis on the statistical-mechanical basis of the law of corresponding states in evaluating both thermostatic and transport properties of gases, the statistical-thermodynamic description of the solid and liquid states, and the calculation of thermal and electrical transport in solids.

We owe a great debt of gratitude to students — too many to name — who have generously helped us to improve the successive drafts of the text in the form of class notes. Professors Creighton A. Depew of the University of Washington and Ernest G. Cravalho of the Massachusetts Institute of Technology each provided very helpful and extensive commentaries on the semifinal manuscript. The University of Kentucky contributed heavily to the mechanical burden of preparing the book; Mrs. Linda Boots carried the major task of typing the manuscript; and Mrs. Mardell Haydon and Mrs. Bonnie Turner completed the final revision. We are also grateful to the University of California and Washington State University for many material contributions to completion of the work.

During the course of this effort we have discovered why authors inevitably thank their wives. Their contributions are real, as it turns out. We are very grateful to Di-hwa and to Carol for helping us to find enough peace and quiet within the normal demands of our households to get the task done.

**Chang L. Tien
John H. Lienhard**

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I introduction

SUBJECT OF 1.1 THERMODYNAMICS

Thermodynamics is commonly thought of as that subject which treats the transformation of energy and the accompanying changes in the states of matter. Surely there are few, if any, disciplines that bear more pretentious definitions than this. In its primal concern with energy and matter, thermodynamics lays claim to the attention of all technical people. The scientist and engineer alike must either come to grips with the subject or suffer the severest limitations upon their professional lives.

The name *thermo-dynamics* calls to mind the idea of thermal energy in transition. The subject is so named because it describes the effects of the dynamic phenomena of heat and work upon systems. The name is misleading insofar as the methods of classical thermodynamics can only describe systems in equilibrium. When a system undergoes a process, classical thermodynamics can do no more than describe the action in terms of static end conditions. In particular, it discloses nothing about the rate of real processes.

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The fact that our subject has grown up under the name of *thermodynamics* is related to an accident of history that profoundly influenced its subsequent development — a matter we shall say more about in Sec. 1.3. Lately, the names *thermostatistics*, *equilibrium thermodynamics*, and *reversible thermodynamics* have been proposed as more descriptive and accurate titles. Their use has been encouraged by the development of the subject of *irreversible thermodynamics*, or *nonequilibrium thermodynamics*, or simply *thermodynamics* (in contrast to thermostatistics). On the macroscopic level this latter subject is concerned with coupled transport processes such as the simultaneous flows of heat and electrical current in a thermocouple.

But our concern is with learning the gross thermodynamic and thermodynamic behavior of systems in terms of the microscopic phenomena in which such behavior has its origins. The present study of statistical thermodynamics will accordingly give greatest emphasis to those manifestations of the *general microscopic behavior* of matter that are thermodynamic in nature.

NATURE OF STATISTICAL 1.2 THERMODYNAMICS

The laws of macroscopic thermodynamics clearly must arise out of the microscopic action of myriads of atoms or other particles. In seeking to determine how these laws arise, we might be tempted to embark upon the straightforward prediction of the action of the individual molecules in a group of molecules in the following way.

Let a large number, N , of particles occupy a box. For each particle we must write a second-order differential equation of motion,

$$\sum_j \mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j, t) = m_i \frac{d^2 \mathbf{r}_i}{dt^2}$$

where \mathbf{r}_i and \mathbf{r}_j are the position vectors of the i th and j th particles, m_i is the mass of the i th particle, and t is time. $\mathbf{F}_{ij}(\mathbf{r}_i, \mathbf{r}_j, t)$ is the complicated force of interaction exerted on the i th particle under consideration by the j th particle and the container walls. Each of these N coupled equations requires two initial conditions,

$$\mathbf{r}_i = \mathbf{a} \quad \text{and} \quad \dot{\mathbf{r}}_i = \mathbf{b} \quad \text{when } t = 0$$

If N were small, this problem could be done on a computer. However, N is on the order of 10^{15} to 10^{30} molecules in real physical systems of interest. Even the most modern digital computers could not begin to solve a problem of such complexity.¹

¹Another impediment to this attack is the fact that the *Heisenberg Uncertainty Principle* precludes the precise simultaneous knowledge of \mathbf{r}_i and $\dot{\mathbf{r}}_i$ at the instant $t = 0$. This is discussed in Sec. 4.5.

But there is a far more important reason why such a straightforward attack upon the problem cannot be fruitful. Such a complete *description of individual particle action would not disclose the gross thermodynamical behavior in which we are interested*. It would reveal only the trees, not the forest.

Clearly, the detailed information about particle behavior must be blurred in some way if a meaningful description of gross behavior is to be obtained. This is what our physical senses do for us automatically when we experience any physical behavior. The physical size of organized animal life is, in fact, determined on this basis. The smallest neural component of an animal must be large with respect to molecular dimensions if it is to respond to average molecular behavior. Otherwise it would respond to the action of individual molecules and behave in a chaotic way.² Conversely, we can be sure that any physical system that we *experience directly* is composed of an immense number of particles.

The problem is then for us to develop analytical methods for describing physical systems in the way that our senses describe the physical world to us. We must develop techniques for averaging the behavior of small particles so that, by ignoring detail, we can discover the gross effects of detail. Just as an insurance company need be concerned only with the most probable vital statistics of its policyholders and can ignore their individual characteristics, we need only determine the most probable behavior of large groups of molecules and can ignore their individual dynamics.

Statistical thermodynamics is the study of the techniques for doing this. It is usually regarded as being composed of two subdivisions: *statistical mechanics* and *kinetic theory*. This division is not sharp because both subdivisions are founded upon similar axiomatic structures.

Statistical mechanics is based on the idea that the equilibrium state of a thermodynamic medium is the macroscopic state that corresponds with the most probable microscopic state. The problem of statistical mechanics is that of determining what microscopic state is most probable; and the results of statistical mechanics, like those of classical thermodynamics, are applicable only to equilibrium configurations.

The kinetic theory employs a somewhat more direct attempt to average the behavior of individual particles. It takes into account definite molecular models and the mechanical details of the motion of individual particles. It is characteristically more complicated, but less abstract, than statistical mechanics. The great advantage of

²This matter is discussed and amplified by E. Schrödinger in *What Is Life? and Other Scientific Essays*, Doubleday & Co., Inc., Garden City, N.Y., 1956, "What Is Life?."