CHANG L. TIEN
JOHN H. LIENHARD

Statistical Thermodynamics

REVISED PRINTING

SERIES IN THERMAL AND FLUIDS ENGINEERING

Statistical Thermodynamics
Revised Printing

CHANG L. TIEN University of California, Berkeley
JOHN H. LIENHARD University of Kentucky

HEMISPHERE PUBLISHING CORPORATION
Washington London

McGRAW-HILL BOOK COMPANY
New York St. Louis San Francisco Auckland Bogotá
Düsseldorf Johannesburg London Madrid Mexico
Montreal New Delhi Panama Paris São Paulo
Singapore Sydney Tokyo Toronto

STATISTICAL THERMODYNAMICS

1 2 3 4 5 6 7 8 9 0 KPKP 7 8 3 2 1 0 9 8

Library of Congress Cataloging in Publication Data

Tien, Chang L date
Statistical thermodynamics.

(Series in thermal and fluids engineering)
Includes bibliographical references and index.
1. Statistical thermodynamics. I. Lienhard, John H., date joint author. II. Title.
QC311.5.T54 1978 536'.7'015195 77-16783

ISBN 0-07-064570-1

Statistical Thermodynamics

SERIES IN THERMAL AND FLUIDS ENGINEERING

JAMES P. HARTNETT and THOMAS F. IRVINE, JR., Editors
JACK P. HOLMAN, Senior Consulting Editor

Cebeci and Bradshaw	• Momentum Transfer in Boundary Layers
Chang	• Control of Flow Separation: Energy Conservation, Operational Efficiency, and Safety
Chi	• Heat Pipe Theory and Practice: A Sourcebook
Eckert and Goldstein	• Measurements in Heat Transfer, 2d edition
Edwards, Denny, and Mills	• Transfer Processes: An Introduction to Diffusion, Convection, and Radiation
Fitch and Surjaatmadja	• Introduction to Fluid Logic
Ginoux	• Two-Phase Flows and Heat Transfer with Application to Nuclear Reactor Design Problems
Hsu and Graham	• Transport Processes in Boiling and Two-Phase Systems, Including Near-Critical Fluids
Kestin	• A Course in Thermodynamics, revised printing
Kreith and Kreider	• Principles of Solar Engineering
Lu	• Introduction to the Mechanics of Viscous Fluids
Moore and Sieverding	• Two-Phase Steam Flow in Turbines and Separators: Theory, Instrumentation, Engineering
Nogotov	• Applications of Numerical Heat Transfer
Richards	• Measurement of Unsteady Fluid Dynamic Phenomena
Sparrow and Cess	• Radiation Heat Transfer, augmented edition
Tien and Lienhard	• Statistical Thermodynamics, revised printing
Wirz and Smolderen	• Numerical Methods in Fluid Dynamics

PROCEEDINGS

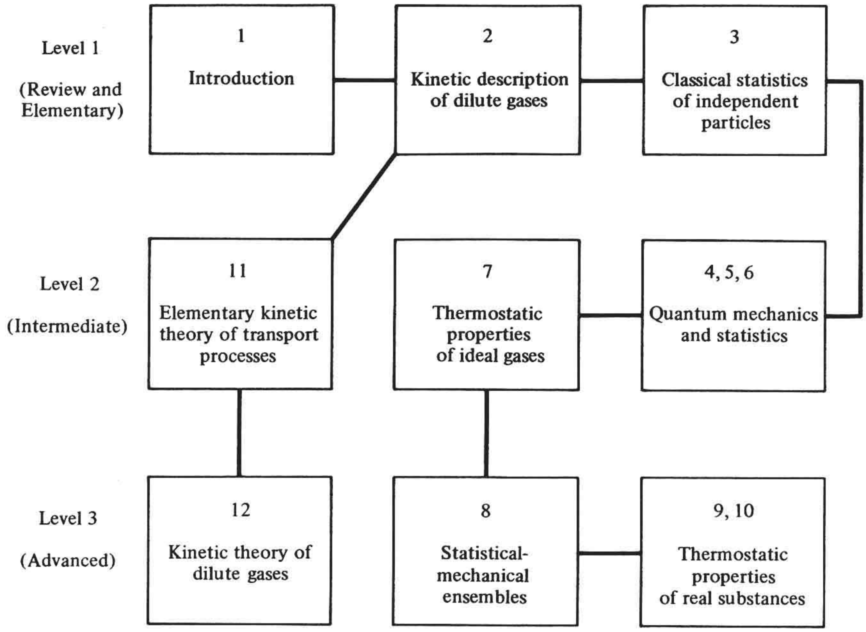
Hoogendoorn and Afgan	• Energy Conservation in Heating, Cooling, and Ventilating Buildings: Heat and Mass Transfer Techniques and Alternatives
Keairns	• Fluidization Technology
Spalding and Afgan	• Heat Transfer and Turbulent Buoyant Convection: Studies and Applications for Natural Environment, Buildings, Engineering Systems
Zarić	• Thermal Effluent Disposal from Power Generation

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 pedagogical 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

Statistical Thermodynamics

Contents