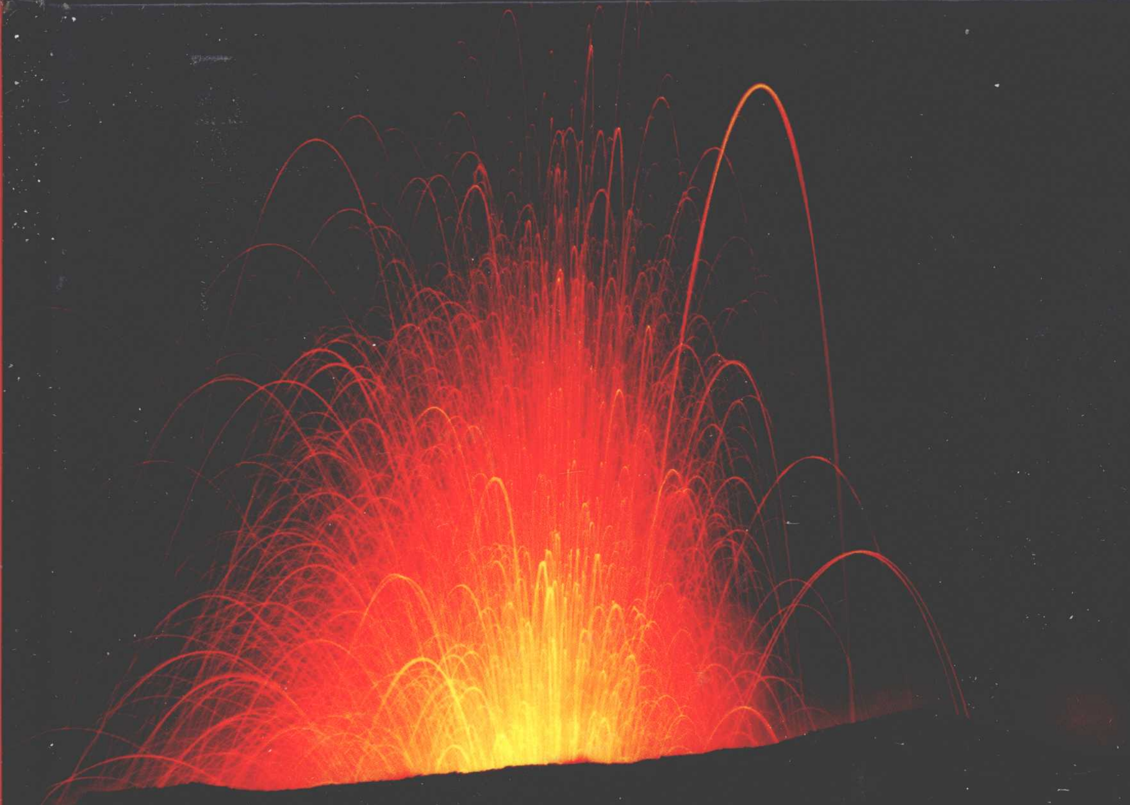

An Introduction to Statistical Mechanics and Thermodynamics

Robert H. Swendsen

FORD GRADUATE TEXTS

An Introduction to Statistical Mechanics and Thermodynamics

Robert H. Swendsen

OXFORD
UNIVERSITY PRESS

OXFORD
UNIVERSITY PRESS

Great Clarendon Street, Oxford OX2 6DP

Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship,
and education by publishing worldwide in

Oxford New York

Auckland Cape Town Dar es Salaam Hong Kong Karachi
Kuala Lumpur Madrid Melbourne Mexico City Nairobi
New Delhi Shanghai Taipei Toronto

With offices in

Argentina Austria Brazil Chile Czech Republic France Greece
Guatemala Hungary Italy Japan Poland Portugal Singapore
South Korea Switzerland Thailand Turkey Ukraine Vietnam

Published in the United States
by Oxford University Press Inc., New York

First published 2012

British Library Cataloguing in Publication Data
Data available

Library of Congress Cataloging in Publication Data
Library of Congress Control Number: 2011945381

Typeset by SPI Publisher Services, Pondicherry, India
Printed and bound by
CPI Group (UK) Ltd, Croydon, CR0 4YY

ISBN 978–0–19–964694–4

1 3 5 7 9 10 8 6 4 2

An Introduction to Statistical Mechanics and Thermodynamics

To the memory of Herbert B. Callen, physicist and mentor,
and to my wife, Roberta L. Klatzky,
without whom this book could never have been written

Preface

Habe Muth dich deines eigenen Verstandes zu bedienen.
(Have the courage to think for yourself.)
Immanuel Kant, in *Beantwortung der Frage: Was ist Aufklärung?*

The disciplines of statistical mechanics and thermodynamics are very closely related, although their historical roots are separate. The founders of thermodynamics developed their theories without the advantage of contemporary understanding of the atomic structure of matter. Statistical mechanics, which is built on this understanding, makes predictions of system behavior that lead to thermodynamic rules. In other words, statistical mechanics is a conceptual precursor to thermodynamics, although it is an historical latecomer.

Unfortunately, despite their theoretical connection, statistical mechanics and thermodynamics are often taught as separate fields of study. Even worse, thermodynamics is usually taught first, for the dubious reason that it is older than statistical mechanics. All too often the result is that students regard thermodynamics as a set of highly abstract mathematical relationships, the significance of which is not clear.

This book is an effort to rectify the situation. It presents the two complementary aspects of thermal physics as a coherent theory of the properties of matter. My intention is that after working through this text a student will have solid foundations in both statistical mechanics and thermodynamics that will provide direct access to modern research.

Guiding Principles

In writing this book I have been guided by a number of principles, only some of which are shared by other textbooks in statistical mechanics and thermodynamics.

- I have written this book for students, not professors. Many things that experts might take for granted are explained explicitly. Indeed, student contributions have been essential in constructing clear explanations that do not leave out 'obvious' steps that can be puzzling to someone new to this material.
- The goal of the book is to provide the student with conceptual understanding, and the problems are designed in the service of this goal. They are quite challenging, but the challenges are primarily conceptual rather than algebraic or computational.
- I believe that students should have the opportunity to program models themselves and observe how the models behave under different conditions. Therefore, the problems include extensive use of computation.

- The book is intended to be accessible to students at different levels of preparation. I do not make a distinction between teaching the material at the advanced undergraduate and graduate levels, and indeed, I have taught such a course many times using the same approach and much of the same material for both groups. As the mathematics is entirely self-contained, students can master all of the material even if their mathematical preparation has some gaps. Graduate students with previous courses on these topics should be able to use the book with self-study to make up for any gaps in their training.
- After working through this text, a student should be well prepared to continue with more specialized topics in thermodynamics, statistical mechanics, and condensed-matter physics.

Pedagogical Principles

The over-arching goals described above result in some unique features of my approach to the teaching of statistical mechanics and thermodynamics, which I think merit specific mention.

Teaching Statistical Mechanics

- The book begins with *classical* statistical mechanics to postpone the complications of quantum measurement until the basic ideas are established.
- I have defined ensembles in terms of probabilities, in keeping with Boltzmann's vision. In particular, the discussion of statistical mechanics is based on Boltzmann's 1877 definition of entropy. This is not the definition usually found in textbooks, but what he actually wrote. The use of Boltzmann's definition is one of the key features of the book that enables students to obtain a deep understanding of the foundations of both statistical mechanics and thermodynamics.
- A self-contained discussion of probability theory is presented for both discrete and continuous random variables, including all material needed to understand basic statistical mechanics. This material would be superfluous if the physics curriculum were to include a course in probability theory, but unfortunately, that is not usually the case. (A course in statistics would also be very valuable for physics students—but that is another story.)
- Dirac delta functions are used to formulate the theory of continuous random variables, as well as to simplify the derivations of densities of states. This is not the way mathematicians tend to introduce probability densities, but I believe that it is by far the most useful approach for scientists.
- Entropy is presented as a logical consequence of applying probability theory to systems containing a large number of particles, instead of just an equation to be memorized.
- The entropy of the classical ideal gas is derived in detail. This provides an explicit example of an entropy function that exhibits all the properties postulated in thermodynamics. The example is simple enough to give every detail of the derivation of thermodynamic properties from statistical mechanics.

- The book includes an explanation of Gibbs' paradox—which is not really paradoxical when you begin with Boltzmann's 1877 definition of the entropy.
- The apparent contradiction between observed irreversibility and time-reversal-invariant equations of motion is explained. I believe that this fills an important gap in a student's appreciation of how a description of macroscopic phenomena can arise from statistical principles.

Teaching Thermodynamics

- The four fundamental postulates of thermodynamics proposed by Callen have been reformulated. The result is a set of six thermodynamic postulates, sequenced so as to build conceptual understanding.
- Jacobians are used to simplify the derivation of thermodynamic identities.
- The thermodynamic limit is discussed, but the validity of thermodynamics and statistical mechanics does not rely on taking the limit of infinite size. This is important if thermodynamics is to be applied to real systems, but is sometimes neglected in textbooks.
- My treatment includes thermodynamics of non-extensive systems. This allows me to include descriptions of systems with surfaces and systems enclosed in containers.

Organization and Content

The principles I have described above lead me to an organization for the book that is quite different from what has become the norm. As was stated above, while most texts on thermal physics begin with thermodynamics for historical reasons, I think it is far preferable from the perspective of pedagogy to begin with statistical mechanics, including an introduction to those parts of probability theory that are essential to statistical mechanics.

To postpone the conceptual problems associated with quantum measurement, the initial discussion of statistical mechanics in Part I is limited to classical systems. The entropy of the classical ideal gas is derived in detail, with a clear justification for every step. A crucial aspect of the explanation and derivation of the entropy is the use of Boltzmann's 1877 definition, which relates entropy to the probability of a macroscopic state. This definition provides a solid, intuitive understanding of what entropy is all about. It is my experience that after students have seen the derivation of the entropy of the classical ideal gas, they immediately understand the postulates of thermodynamics, since those postulates simply codify properties that they have derived explicitly for a special case.

The treatment of statistical mechanics paves the way to the development of thermodynamics in Part II. While this development is largely based on the classic work by Herbert Callen (who was my thesis advisor), there are significant differences. Perhaps the most important is that I have relied entirely on Jacobians to derive thermodynamic identities. Instead of regarding such derivations with dread—as I did when I first encountered them—my students tend to regard them as straightforward and rather easy. There are also several other changes in emphasis, such as a clarification of the postulates of thermodynamics and the inclusion of non-extensive systems; that is, finite systems that have surfaces or are enclosed in containers.

Part III returns to classical statistical mechanics and develops the general theory directly, instead of using the common roundabout approach of taking the classical limit of quantum statistical mechanics. A chapter is devoted to a discussion of the apparent paradoxes between microscopic reversibility and macroscopic irreversibility.

Part IV presents quantum statistical mechanics. The development begins by considering a probability distribution over all quantum states, instead of the common *ad hoc* restriction to eigenstates. In addition to the basic concepts, it covers black-body radiation, the harmonic crystal, and both Bose and Fermi gases. Because of their practical and theoretical importance, there is a separate chapter on insulators and semiconductors. The final chapter introduces the Ising model of magnetic phase transitions.

The book contains about a hundred multi-part problems that should be considered as part of the text. In keeping with the level of the text, the problems are fairly challenging, and an effort has been made to avoid 'plug and chug' assignments. The challenges in the problems are mainly due to the probing of essential concepts, rather than mathematical complexities. A complete set of solutions to the problems is available from the publisher.

Several of the problems, especially in the chapters on probability, rely on computer simulations to lead students to a deeper understanding. In the past I have suggested that my students use the C++ programming language, but for the last two years I have switched to VPython for its simplicity and the ease with which it generates graphs. An introduction to the basic features of VPython is given in in Appendix A. Most of my students have used VPython, but a significant fraction have chosen to use a different language—usually Java, C, or C++. I have not encountered any difficulties with allowing students to use the programming language of their choice.

Two Semesters or One?

The presentation of the material in this book is based primarily on a two-semester undergraduate course in thermal physics that I have taught several times at Carnegie Mellon University. Since two-semester undergraduate courses in thermal physics are rather unusual, its existence at Carnegie Mellon for several decades might be regarded as surprising. In my opinion, it should be the norm. Although it was quite reasonable to teach two semesters of classical mechanics and one semester of thermodynamics to undergraduates in the nineteenth century—the development of statistical mechanics was just beginning—it is not reasonable in the twenty-first century.

However, even at Carnegie Mellon only the first semester of thermal physics is required. All physics majors take the first semester, and about half continue on to the second semester, accompanied by a few students from other departments. When I teach the course, the first semester covers the first two parts of the book (Chapters 1 through 18), plus an overview of classical canonical ensembles (Chapter 18) and quantum canonical ensembles (Chapter 22). This gives the students an introduction to statistical mechanics and a rather thorough knowledge of thermodynamics, even if they do not take the second semester.

It is also possible to teach a one-semester course in thermal physics from this book using different choices of material. For example:

- If the students have a strong background in probability theory (which is, unfortunately, fairly rare), Chapters 3 and 5 might be skipped to include more material in Parts III and IV.
- If it is decided that students need a broader exposure to statistical mechanics, but that a less detailed study of thermodynamics is sufficient, Chapters 14 through 17 could be skimmed to have time to study selected chapters in Parts III and IV.
- If the students have already had a thermodynamics course (although I do not recommend this course sequence), Part II could be skipped entirely. However, even if this choice is made, students might still find Chapters 9 to 18 useful for review.

One possibility that I do not recommend would be to skip the computational material. I am strongly of the opinion that the undergraduate physics curricula at most universities still contain too little instruction in the computational methods that students will need in their careers.

Acknowledgments

This book was originally intended as a resource for my students in Thermal Physics I (33-341) and Thermal Physics II (33-342) at Carnegie Mellon University. In an important sense, those students turned out to be essential collaborators in its production.

I would like to thank the many students from these courses for their great help in suggesting improvements and correcting errors in the text. All of my students have made important contributions. Even so, I would like to mention explicitly the following students: Michael Alexovich, Dimitry Ayzenberg, Conroy Baltzell, Anthony Bartolotta, Alexandra Beck, David Bemiller, Alonzo Benavides, Sarah Benjamin, John Briguglio, Coleman Broaddus, Matt Buchovecky, Luke Ceurvorst, Jennifer Chu, Kunting Chua, Charles Wesley Cowan, Charles de las Casas, Matthew Daily, Brent Driscoll, Luke Durback, Alexander Edelman, Benjamin Ellison, Danielle Fisher, Emily Gehrels, Yelena Goryunova, Benjamin Greer, Nils Guillermin, Asad Hasan, Aaron Henley, Maxwell Hutchinson, Andrew Johnson, Agnieszka Kalinowski, Patrick Kane, Kamran Karimi, Joshua Keller, Deena Kim, Andrew Kojzar, Rebecca Krall, Vikram Kulkarni, Avishek Kumar, Anastasia Kurnikova, Thomas Lambert, Grant Lee, Robert Lee, Jonathan Long, Sean Lubner, Alan Ludin, Florence Lui, Christopher Magnollay, Alex Marakov, Natalie Mark, James McGee, Andrew McKinnie, Jonathan Michel, Corey Montella, Javier Novales, Kenji Oman, Justin Perry, Stephen Poniatowicz, Thomas Prag, Alisa Rachubo, Mohit Raghunathan, Peter Ralli, Anthony Rice, Svetlana Romanova, Ariel Rosenburg, Matthew Rowe, Kaitlyn Schwalje, Omar Shams, Gabriella Shepard, Karpur Shukla, Stephen Sigda, Michael Simms, Nicholas Steele, Charles Swanson, Shaun Swanson, Brian Tabata, Likun Tan, Joshua Tepper, Kevin Tian, Eric Turner, Joseph Vukovich, Joshua Watzman, Andrew Wesson, Justin Winokur, Nanfei Yan, Andrew Yeager, Brian Zakrzewski, and Yuriy Zubovski. Some of these students made particularly important contributions, for which I have thanked them personally. My students' encouragement and suggestions have been essential in writing this book.

Yutaro Iiyama and Marilia Cabral Do Rego Barros have both assisted with the grading of Thermal Physics courses, and have made very valuable corrections and suggestions.

The last stages in finishing the manuscript were accomplished while I was a guest at the Institute of Statistical and Biological Physics at the Ludwig-Maximilians-Universität, Munich, Germany. I would like to thank Prof. Dr. Erwin Frey and the other members of the Institute for their gracious hospitality.

Throughout this project, the support and encouragement of my friends and colleagues Harvey Gould and Jan Tobochnik have been greatly appreciated.

I would also like to thank my good friend Lawrence Erlbaum, whose advice and support have made an enormous difference in navigating the process of publishing a book.

Finally, I would like to thank my wife, Roberta (Bobby) Klatzky, whose contributions are beyond count. I could not have written this book without her loving encouragement, sage advice, and relentless honesty.

My thesis advisor, Herbert Callen, first taught me that statistical mechanics and thermodynamics are fascinating subjects. I hope you come to enjoy them as much as I do.

Robert H. Swendsen

Pittsburgh, January 2011

Contents

Part II Thermodynamics

Part IV Quantum Statistical Mechanics