Foundations of Statistical Mechanics

Volume I:
Equilibrium Theory

Fundamental Theories of Physics

A New International Book Series on The Fundamental Theories of Physics: Their Clarification, Development and Application

Foundations of Statistical Mechanics

Volume I: Equilibrium Theory

by

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For my Chauffeur

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Preface

In a certain sense this book has been twenty-five years in the writing, since I first struggled with the foundations of the subject as a graduate student. It has taken that long to develop a deep appreciation of what Gibbs was attempting to convey to us near the end of his life and to understand fully the same ideas as resurrected by E.T. Jaynes much later. Many classes of students were destined to help me sharpen these thoughts before I finally felt confident that, for me at least, the foundations of the subject had been clarified sufficiently.

More than anything, this work strives to address the following questions: What *is* statistical mechanics? Why is this approach so extraordinarily effective in describing bulk matter in terms of its constituents? The response given here is in the form of a very definite point of view—the principle of maximum entropy (PME). There have been earlier attempts to approach the subject in this way, to be sure, reflected in the books by Tribus [*Thermostatics and Thermodynamics*, Van Nostrand, 1961], Baierlein [*Atoms and Information Theory*, Freeman, 1971], and Hobson [*Concepts in Statistical Mechanics*, Gordon and Breach, 1971]. Despite these efforts the bulk of writers on the subject, though diminishing in number, still fail to appreciate that statistical mechanics is a special case of a general reasoning process that appears to be optimal when insufficient information is available. This point of view was implicit in Boltzmann's later writings, and certainly was made explicit by Gibbs. The lasting contributions by these fathers of the subject lie with development of new methods of analysis, not in the discovery of new physics. Unfortunately, the exciting new physics was just coming to life as they passed from the scene.

It is apparent that the subjects of statistical mechanics and thermodynamics can mean many things to many different people. Indeed, the subjects tend to arouse deep emotions in a way unfamiliar to other areas of physics. One need only recall the tribulations of Robert Mayer circa 1840 in attempting to establish the first law of thermodynamics in conjunction with energy conservation: for his efforts he was ostracized in the community, his medical practice ruined, and even his attempts at suicide ended in failure! Planck recorded his own despair in his scientific autobiography. Similarly, the maximum-entropy principle, though advocated in one form or another since Boltzmann, continues to be pilloried in some quarters, and even characterized as 'muddleheaded' and 'nonsense'. Although a distinct minority, there nevertheless are those whose very vocal response to any new attempts at deeper insight in this area is scalding and charged with emotion—and to whose discomfort this volume will no doubt contribute immensely. Much of the rhetoric has already been answered by Jaynes in his collected works on these topics [*E.T. Jaynes: Papers on Probability, Statistics and Statistical Physics*, Reidel, 1983], so that little more in the way of polemic will be offered here.

Rather, a great deal of space is devoted to discussing what statistical mechanics is, and is not. For this reason the reader may encounter in the early chapters a number of topics deemed elementary for what is generally a somewhat advanced book, but the author has found it necessary to re-examine such topics in order to maintain a certain coherence in the discussion. Consequently, the first three chapters can be, and in fact have been used as a basis for undergraduate lectures. But the whole is directed toward the advanced undergraduate and graduate student, with a general emphasis on quantum statistical mechanics.

The topics treated throughout the book have been chosen to elucidate the *foundations* of the subject—that, after all, is the major thrust of the work. But the foundations can hardly be made clear without a number of detailed applications. Some of the latter tend to be a bit different than found in the usual textbook, and may possibly yield some new insights.

Unquestionably the student will not find here *all* the tools needed in order to carry out professional research in the field. For example, numerical techniques, such as the Monte-Carlo method, are essentially mentioned only in passing, and path-integral methods do not receive even that much notice. It is not the intent of the work to provide the wealth of calculational detail to be found in Fetter and Walecka [*Quantum Theory of Many-Particle Systems*, McGraw-Hill, 1971], say. Rather, an attempt is made to provide some answers to the questions raised at the beginning, from what some may consider a non-standard view. If the book serves to generate some non-standard thought along these lines as well, one of its purposes will have been achieved. In addition, it is also meant to serve as a foundation for Volume II, in which the much more exciting topics of nonequilibrium phenomena are addressed.

As a text, the book forms the basis for a solid one-semester introductory course at the senior/graduate level. Although a number of problems have been included, they have been chosen mainly to illustrate the discussion in the text. Many more standard problems, particularly of the detailed calculational variety, are known and available to most lecturers in statistical mechanics.

I have attempted to include copious and detailed references, including those relevant to the historical record. Moreover, this is one aspect which is somewhat novel to the literature of physics, in that an attempt has been made to verify and supply the *titles* of all referenced works. Unfortunately, after all is said and done there are still a few missing—but not many. Aside from scholarly interest, my aim is to encourage such practice in this field, because it is eminently useful to the reader—and sometimes even to the writer!

There are numerous people who have contributed to the completion of this work, either directly or indirectly. Although it is not possible to provide detailed acknowledgment here, a few nevertheless will have to bear public exposure. It is only stating the obvious when I point to the extraordinary influence Ed Jaynes has had on my thoughts about the foundations of statistical mechanics. His friendship, good humor, and collegiality over many years have been greatly appreciated.

I have long been indebted to Franz Mohling for initially stimulating my interest in statistical mechanics and continuing to generate enthusiasm through thoughtful debate. I shall forever regret that he died without seeing this finished product, for I believe that he had come to share a great many of the views expressed here. After insisting that I stop climbing mountains and finish my dissertation, he climbed one too many himself.

Locating and identifying many older references would have been significantly more tedious without the generous assistance of Professor Lewis Pyenson, Université de Montréal, for which I am grateful. Professor John Skilling of Cambridge University provided thoughtful criticism of Chapter 2; no doubt some criticisms remain, but it is a better discussion for having suffered his scrutiny. Finally, it is customary at this point to thank typists and editors for their heroic efforts—but there are none! This entire book was *typeset* by the author using the marvelous typesetting program TeX developed by Donald Knuth. On the one

hand, availability of computerized typesetting with microcomputers has introduced a great deal of flexibility on the part of authors in producing highly technical books of this kind. On the other hand, the publisher is now granted significant absolution, so that essentially any and all defects are solely my responsibility.

W.T. Grandy, Jr.

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