

# Foundations of Statistical Mechanics

Volume I:  
Equilibrium Theory

# Fundamental Theories of Physics

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# Foundations of Statistical Mechanics

## Volume I: Equilibrium Theory

*by*

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*For my Chauffeur*

# Contents

<i>Preface</i>	<i>ziii</i>
<b>Chapter 1</b>	
<b>Introduction</b>	<b>1</b>
A. Physical Foundations	2
Many Degrees of Freedom	9
B. Kinetic Theory	13
C. The Notion of Ensembles	19
D. Ergodic Theory	24
E. Critique	26
Problems	27
References	28
<b>Chapter 2</b>	
<b>Theory of Probability</b>	<b>31</b>
A. Historical Background	31
B. The Algebra of Probable Inference	34
Axiomatic Formulation	35
Extensions of the Theory	41
Probabilities and Frequencies	45
C. Calculus of Probable Inference	48
Principle of Maximum Entropy	49
Further Properties of $S_I$	54
Probabilities and Frequencies	56
General Observations	59
Problems	59
References	61
<b>Chapter 3</b>	
<b>Equilibrium Thermodynamics</b>	<b>64</b>
A. Canonical Ensemble	64
B. Fluctuations	68
Measured Values	70
Measurable Fluctuations	71
Stability of the Equilibrium State	72
C. The Efficacy of Statistical Mechanics	73
Macroscopic Uniformity	75

Generalized Inverse Problems	77
Infinite Volume Limit	79
Problems	81
References	82
<b>Chapter 4</b>	
<b>Quantum Statistical Mechanics</b>	84
A. Review of the Principles of Quantum Mechanics	84
B. Principle of Maximum Entropy	88
The Entropy	88
The PME	92
C. Grand Canonical Ensemble	95
Single-Component Systems	98
Many-Body Quantum Mechanics	101
The Necessity of Quantum Statistics	103
Pressure Ensemble	105
Summary	106
D. Physical Entropy and the Second Law of Thermodynamics	108
Classical Background	108
The Theoretical Connection	110
Physical Interpretation	112
Irreversibility	113
E. Space-Time Transformations	114
Rotations	117
Galilean Transformations	117
Lorentz Transformations	118
Relativistic Statistical Mechanics	119
Problems	120
References	121
<b>Chapter 5</b>	
<b>Noninteracting Particles</b>	124
A. Free-Particle Models	124
Historical Observations	128
B. Boltzmann Statistics	130
Weak Degeneracy	133
C. The Degenerate Fermi Gas	135
D. The Degenerate Bose Gas	138
The Photon Gas	144
E. Relativistic Statistics	147
Weak Degeneracy	150
Degenerate Fermions	151
Bose-Einstein Condensation	154
The Function $f(x)$	156
Problems	157
References	158

**Chapter 6****External Fields**

	161
A. Inhomogeneous Systems in Equilibrium	161
Uniformly Rotating Bucket	163
Uniform Gravitational Field	164
Harmonic Confinement	165
Bose-Einstein Condensation in a Gravitational Field	167
B. 'Classical Magnetism'	169
Paramagnetism	171
Diamagnetism	173
The Importance of Quantum Mechanics	176
C. Quantum Theory of Magnetism	176
Spinless Bosons	178
Degenerate Electron Gas	182
High-Field Pauli Paramagnetism	185
D. Relativistic Paramagnetism	189
Degenerate Equation of State	189
Ground-State Magnetization	192
Evaluation of the Integrals $J_1$ and $J_2$	193
Problems	194
References	195

**Chapter 7****Interacting Particles I:****Classical and Quantum Clustering**

	197
A. Cluster Integrals and the Method of Ursell	197
The Symmetry Problem	201
B. Virial Expansion of the Equation of State	204
Inversion of the Fugacity Expansion	205
Ideal Quantum Gases	208
The Virial Coefficients	209
C. Classical Virial Coefficients	213
Hard Spheres	218
Point Centers of Repulsion-Soft Spheres	218
Repulsive Exponential	220
Hard Core Plus Square Well	221
Sutherland Potential	222
Triangle Well	222
Trapezoidal Well	223
Lennard-Jones Potential	223
Miscellaneous Models	224
Experimental Survey	224
D. Quantum Corrections to the Classical Virial Coefficients	225
Hard Spheres	228
Other Models	232
Higher Virial Coefficients and General Results	234



E. Quantum Virial Coefficients	235
Higher Virial Coefficients	238
F. Paramagnetic Susceptibility	239
Problems	242
References	243
<b>Chapter 8</b>	
<b>Interacting Particles, II:</b>	
<b>Fock-Space Formulation</b>	249
A. Particle Creation and Annihilation	249
B. Ground State of the Hard-Sphere Bose Gas	256
C. The Phonon Field	261
Gas of Noninteracting Phonons	263
D. Completely Degenerate Electron Gas	267
E. Digression: A Perturbation Expansion of $f(\beta, \mu; V)$	272
F. Long-Range Forces	278
Coulomb Interactions and Screening	279
Gravitational Interactions	283
Problems	286
References	288
<b>Chapter 9</b>	
<b>The Phases of Matter</b>	290
A. Correlations and the Liquid State	292
Radial Distribution Function	297
Ideal Quantum Fluids	300
Ornstein-Zernike Theory	301
Theory of Liquids	303
B. Crystalline Solids	306
Free-Electron Model	307
Electrons and Phonons	310
C. Phase Transitions	311
Phenomenological Theory	314
Modern Developments	319
D. Superconductivity	325
The BCS Theory	328
Problems	330
References	330
<b>Appendix A</b>	
<b>Highpoints in the History of Statistical Mechanics</b>	337
<b>Appendix B</b>	
<b>The Law of Succession</b>	341
<b>Appendix C</b>	
<b>Method of Jacobians</b>	344

<i>Contents</i>	xi
<b>Appendix D</b>	
<b>Convex Functions and Inequalities</b>	348
<b>Appendix E</b>	
<b>Euler-Maclaurin Summation Formula</b>	360
<b>Appendix F</b>	
<b>The First Four Ursell Functions and Their Inverses</b>	362
<b>Appendix G</b>	
<b>Thermodynamic Form of Wick's Theorem</b>	364
<i>Index</i>	369

# 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 [*Thermostat-ics 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  $\text{\TeX}$  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.

Laramie, Wyoming  
December 1986