Contents

Preface *xiii*

Chapter 1
Introduction 1

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

Chapter 2
Theory of Probability 31

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

Chapter 3
Equilibrium Thermodynamics 64

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

Chapter 4
Quantum Statistical Mechanics 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

Chapter 5
Noninteracting Particles 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 Coeficients 238
F. Paramagnetic Susceptibility 239
Problems 242
References 243

Chapter 8
Interacting Particles, II:
Fock-Space Formulation 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

Chapter 9
The Phases of Matter 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

Appendix A
Highpoints in the History of Statistical Mechanics 337

Appendix B
The Law of Succession 341

Appendix C
Method of Jacobians 344

Appendix D
Convex Functions and Inequalities 348

Appendix E
Euler-Maclaurin Summation Formula 360

Appendix F
The First Four Ursell Functions and Their Inverses 362

Appendix G
Thermodynamic Form of Wick's Theorem 364

Index 369