CONTENTS

PREFACE TO THE SECOND EDITION xi

PREFACE TO THE FIRST EDITION xiii

HISTORICAL INTRODUCTION 1

Notes 6

Chapter 1. *The Statistical Basis of Thermodynamics* 9

1.1. The macroscopic and the microscopic states 9
1.2. Contact between statistics and thermodynamics: physical significance of the number $\Omega(N, V, E)$ 11
1.3. Further contact between statistics and thermodynamics 13
1.4. The classical ideal gas 15
1.5. The entropy of mixing and the Gibbs paradox 22
1.6. The "correct" enumeration of the microstates 25
Problems 26
Notes 28

Chapter 2. *Elements of Ensemble Theory* 30

2.1. Phase space of a classical system 30
2.2. Liouville's theorem and its consequences 32
2.3. The microcanonical ensemble 34
2.4. Examples 36
2.5. Quantum states and the phase space 39
Problems 40
Notes 41

Chapter 3. *The Canonical Ensemble* 43

3.1. Equilibrium between a system and a heat reservoir 44
3.2. A system in the canonical ensemble 45
3.3. Physical significance of the various statistical quantities in the canonical ensemble 53
3.4. Alternative expressions for the partition function 55
3.5. The classical systems 56
3.6. Energy fluctuations in the canonical ensemble: correspondence with the microcanonical ensemble 60

3.7. Two theorems–the "equipartition" and the "virial" 63
3.8. A system of harmonic oscillators 66
3.9. The statistics of paramagnetism 71
3.10. Thermodynamics of magnetic systems: negative temperatures 77
Problems 83
Notes 89

Chapter 4. *The Grand Canonical Ensemble* 90

4.1. Equilibrium between a system and a particle–energy reservoir 90
4.2. A system in the grand canonical ensemble 92
4.3. Physical significance of the various statistical quantities 93
4.4. Examples 96
4.5. Density and energy fluctuations in the grand canonical ensemble: correspondence with other ensembles 100
Problems 102
Notes 103

Chapter 5. *Formulation of Quantum Statistics* 104

5.1. Quantum-mechanical ensemble theory: the density matrix 104
5.2. Statistics of the various ensembles 107
A. The microcanonical ensemble 107
B. The canonical ensemble 109
C. The grand canonical ensemble 110
5.3. Examples 111
A. An electron in a magnetic field 111
B. A free particle in a box 111
C. A linear harmonic oscillator 113
5.4. Systems composed of indistinguishable particles 115
5.5. The density matrix and the partition function of a system of free particles 119
Problems 124
Notes 125

Chapter 6. *The Theory of Simple Gases* 127

6.1. An ideal gas in a quantum-mechanical microcanonical ensemble 127
6.2. An ideal gas in other quantum-mechanical ensembles 131
6.3. Statistics of the occupation numbers 134
6.4. Kinetic considerations 137
6.5. Gaseous systems composed of molecules with internal motion 140
A. Monatomic molecules 141
B. Diatomic molecules 142
C. Polyatomic molecules 150
Problems 152
Notes 155

Chapter 7. *Ideal Bose Systems* 157

7.1. Thermodynamic behavior of an ideal Bose gas 158
7.2. Thermodynamics of the black-body radiation 168
7.3. The field of sound waves 172
7.4. Inertial density of the sound field 179
7.5. Elementary excitations in liquid helium II 182
Problems 188
Notes 193

Chapter 8. *Ideal Fermi Systems* 195

8.1. Thermodynamic behavior of an ideal Fermi gas 195
8.2. Magnetic behavior of an ideal Fermi gas 201
A. Pauli paramagnetism 202
B. Landau diamagnetism 206
8.3. The electron gas in metals 209
A. Thermionic emission (the Richardson effect) 213
B. Photoelectric emission (the Hallwachs effect) 216
8.4. Statistical equilibrium of white dwarf stars 219
8.5. Statistical model of the atom 223
Problems 227
Notes 231

Chapter 9. *Statistical Mechanics of Interacting Systems: The Method of Cluster Expansions* 232

9.1. Cluster expansion for a classical gas 232
9.2. Virial expansion of the equation of state 239
9.3. Evaluation of the virial coefficients 240
9.4. General remarks on cluster expansions 245
9.5. Exact treatment of the second virial coefficient 249
9.6. Cluster expansion for a quantum-mechanical system 254
Problems 259
Notes 261

Chapter 10. *Statistical Mechanics of Interacting Systems: The Method of Quantized Fields* 262

10.1. The formalism of second quantization 262
10.2. Low-temperature behavior of an imperfect Bose gas 270
10.3. Low-lying states of an imperfect Bose gas 273
10.4. Energy spectrum of a Bose liquid 277
10.5. States with quantized circulation 280
10.6. Quantized vortex rings and the breakdown of superfluidity 285
10.7. Low-lying states of an imperfect Fermi gas 289
10.8. Energy spectrum of a Fermi liquid: Landau's phenomenological theory 293
Problems 299
Notes 302

Chapter 11. Phase Transitions: Criticality, Universality and Scaling 305

11.1. General remarks on the problem of condensation 306
11.2. Condensation of a van der Waals gas 310
11.3. A dynamical model of phase transitions 314
11.4. The lattice gas and the binary alloy 319
11.5. Ising model in the zeroth approximation 321
11.6. Ising model in the first approximation 328
11.7. The critical exponents 334
11.8. Thermodynamic inequalities 338
11.9. Landau's phenomenological theory 341
11.10. Scaling hypothesis for thermodynamic functions 344
11.11. The role of correlations and fluctuations 348
11.12. The critical exponents ν and η 353
11.13. A final look at the mean field theory 356
Problems 359
Notes 364

Chapter 12. Phase Transitions: Exact (or Almost Exact) Results for the Various Models 366

12.1. The Ising model in one dimension 366
12.2. The n-vector models in one dimension 372
12.3. The Ising model in two dimensions 377
12.4. The spherical model in arbitrary dimensions 389
12.5. The ideal Bose gas in arbitrary dimensions 398
12.6. Other models 404
Problems 407
Notes 413

Chapter 13. Phase Transitions: The Renormalization Group Approach 414

13.1. The conceptual basis of scaling 415
13.2. Some simple examples of renormalization 418
A. The Ising model in one dimension 418
B. The spherical model in one dimension 421
C. The Ising model in two dimensions 423
13.3. The renormalization group: general formulation 426
13.4. Applications of the renormalization group 431
A. The Ising model in one dimension 432
B. The spherical model in one dimension 432
C. The Ising model in two dimensions 433
D. The ε-expansion 436
E. The $1/n$ expansion 439
F. Other topics 439
13.5. Finite-size scaling 441
Case A: $T \gtrsim T_c(\infty)$ 443
Case B: $T \simeq T_c(\infty)$ 443
Case C: $T < T_c(\infty)$ 444
Problems 449
Notes 451

Chapter 14. Fluctuations 452

14.1. Thermodynamic fluctuations 453
14.2. Spatial correlations in a fluid 456
14.3. The Einstein–Smoluchowski theory of the Brownian motion 459
14.4. The Langevin theory of the Brownian motion 464
14.5. Approach to equilibrium: the Fokker–Planck equation 469
14.6. Spectral analysis of fluctuations: the Wiener–Khintchine theorem 474
14.7. The fluctuation–dissipation theorem 481
14.8. The Onsager relations 484
Problems 489
Notes 492

APPENDIXES 495

A. Influence of boundary conditions on the distribution of quantum states 495
B. Certain mathematical functions 497
Stirling's formula for $\nu!$ 499
The Dirac δ-function 501
C. "Volume" and "surface area" of an n-dimensional sphere of radius R 504
D. On Bose–Einstein functions 506
E. On Fermi–Dirac functions 508
F. On Watson functions 510
Notes 512

BIBLIOGRAPHY 513
INDEX 523