Table of Contents

Part I. General Foundations

Chapter I. *The Principles of Classical Statistics* 3

§ 1.1. Nature and Problems of Statistical Thermodynamics 3
§ 1.2. Phase Space and Virtual Ensemble. Liouville's Theorem 5
§ 1.3. Canonical Invariance. The Statistical Equilibrium 12
§ 1.4. Axiomatic Foundations I: General Viewpoints 16
§ 1.5. Axiomatic Foundations II: The von Neumann-Birkhoff Theorem 23
§ 1.6. Axiomatic Foundations III: Fermi's Theorem. Discussion of Ergodic Theory 32
§ 1.7. Axiomatic Foundations IV: The Theory of Representative Ensembles . . . 39
§ 1.8. The Semi-Classical Approximation. The Microcanonical Ensemble 42
§ 1.9. The Equipartition Theorem and the Virial Theorem 46
§ 1.10. The Empirical Temperature 49
§ 1.11. The Theorem of Adiabatic Invariance of Phase Volume 50
§ 1.12. Entropy and Absolute Temperature 53
§ 1.13. Explicit Computation of the Entropy 55
§ 1.14. Thermodynamic Equilibrium. Accessibility and Constraints 59
§ 1.15. The Microcanonical Ensemble and μ-Space Statistics. The Maxwell-Boltzmann Distribution Law 62
§ 1.16. The Canonical Ensemble 69

Chapter II. *The Principles of Quantum Statistics* 75

§ 2.1. Quantum Mechanics and Quantum Statistics 75
§ 2.2. The Density Matrix. The Liouville Theorem of Quantum Statistics. Statistical Equilibrium 77
§ 2.3. Macroscopic Variables 85
§ 2.4. Axiomatic Foundations I: The Ergodic Theorem of Quantum Statistics . . 88
§ 2.5. Axiomatic Foundations II: The Hypothesis of Equal a Priori Probabilities and Random Phase Distribution 93
§ 2.6. The Microcanonical Ensemble of Quantum Statistics. The Virial Theorem . 97
§ 2.7. Calculation of Ω for Separable Systems 101
§ 2.8. The Darwin-Fowler Method for Localized Particles 103
§ 2.9. The Darwin-Fowler Method for Non-localized Particles 108
§ 2.10. The Canonical Ensemble of Quantum Statistics 113
§ 2.11. Thermodynamic Analogues 115
§ 2.12. Additivity of Entropy. Equilibrium Conditions (Gibbs' Extremum Theorems) 119
§ 2.13. Partition Function and Slater Sum 123
§ 2.14. Calculation of the Partition Function for Separable Systems 124
§ 2.15. Bloch's Equation 126
§ 2.16. The High Temperature Expansion. The Semi-classical Approximation . . . 134
§ 2.17. The Low Temperature Expansion 137
§ 2.18. The Grand Canonical Ensemble 143
§ 2.19. Computation of the Grand Partition Function 153

Chapter III. *Generalized Ensembles. Fluctuations* 164

§ 3.1. The Second Postulate of Statistical Thermodynamics 164
§ 3.2. Transformation Theory of Partition Functions 168
§ 3.3. Fluctuations of Extensive Parameters 179
§ 3.4. Fluctuations of Intensive Parameters 187
§ 3.5. Fluctuations of Internal Parameters 195
§ 3.6. Phenomenological Theory of Local Fluctuations. Light Scattering by Liquid One-Component Systems 199

Chapter IV. *The General Foundations of Thermodynamics. Phase Transitions* 212
§ 4.1. Statement of the Problem 212
§ 4.2. The Limit Theorem for the Canonical Ensemble 214
§ 4.3. The Limit Theorems for the Grand Canonical Ensemble and the Microcanonical Ensemble 229
§ 4.4. Thermodynamics as an Asymptotic Limiting Case (the Equivalence Problem) 236
§ 4.5. The Thermodynamic Stability Conditions 256
§ 4.6. Phase Transitions I: General Considerations 262
§ 4.7. Phase Transitions II: The Theory of YANG and LEE 268
§ 4.8. Phase Transitions III: Relations to Fluctuation Theory 286
§ 4.9. One-Dimensional Systems I: Interactions between Nearest Neighbors . . . 292
§ 4.10. One-Dimensional Systems II: Interactions between a Finite Number of Neighbors. Van Hove's Theorem 298
§ 4.11. One-Dimensional Systems III: Generalization of the van Hove Theorem. Interactions of Infinite Range 306

Chapter V. *Molecular Distribution Functions* 317
§ 5.1. Definition and General Properties 317
§ 5.2. Application of the Canonical Ensemble 319
§ 5.3. The Integral Equations of YVON, BORN-GREEN and KIRKWOOD. The Superposition Approximation 329
§ 5.4. The Application of the Grand Canonical Ensemble 336
§ 5.5. The Introduction of Normal States. The Cluster Expansion 344
§ 5.6. The Mayer Integral Equations 349
§ 5.7. The Kirkwood Equations of the Second Kind 355
§ 5.8. The Percus Method of Taylor Expansion of Functionals 358
§ 5.9. An Alternative Derivation of the Kirkwood Equations of the Second Kind. The Integral Equation of PERCUS-YEVICK. The Hypernetted-Chain Equation 364
§ 5.10. Phase Changes 370
§ 5.11. The One-Dimensional Liquid 374
§ 5.12. The One-Dimensional Crystal 387
§ 5.13. Molecular Distribution Functions in Quantum Statistics 392
§ 5.14. Molecular Theory of Local Fluctuations. Coarse Grained Correlation Functions. Analysis of Phenomenological Fluctuation Theory 396
§ 5.15. Critical Fluctuations 404

Part II. Theory of Gases

Chapter VI. *Ideal Gases* 419
§ 6.1. Definition and General Properties 419
§ 6.2. Monatomic Molecules 422
§ 6.3. Rotation of Diatomic Molecules 424
§ 6.4. The Influence of Nuclear Spin 426
§ 6.5. Ortho- and Para-hydrogen 430
§ 6.6. The Vibrational Degree of Freedom 435
§ 6.7. The Influence of the Electrons 444
§ 6.8. Gases of Polyatomic Molecules 446
§ 6.9. Rotation of Polyatomic Molecules 449
§ 6.10. Vibrations of Polyatomic Molecules 454
§ 6.11. Internal Rotations of Polyatomic Molecules 462

Chapter VII. *Chemical Equilibrium in Ideal Gases* 476
§ 7.1. Equilibrium between Isomers 476
§ 7.2. General Statistical Theory of Dissociation Equilibrium 477
§ 7.3. The Chemical Constants 483
§ 7.4. Supplementary Remarks on the Theory of Chemical Equilibrium 488

Chapter VIII. *Real Gases at Ordinary Pressures* (Theory of the Second Virial Coefficient) 492
§ 8.1. General Remarks on the Properties of Real Gases. Equations of State . . . 492
§ 8.2. Statistical Theory of the Second Virial Coefficient 496

§ 8.3. The Second Virial Coefficient and Intermolecular Forces. Experimental Test of the Theory 498
§ 8.4. Quantum Statistical Theory of the Second Virial Coefficient 518
§ 8.5. The Law of Corresponding States 532

Chapter IX. *General Theory of Real Gases* 537

§ 9.1. Cluster Integrals 537
§ 9.2. The Irreducible Cluster Integrals 542
§ 9.3. The Introduction of the Grand Partition Function 547
§ 9.4. The Virial Form of the Equation of State. Thermodynamic Properties of Real Gases 549
§ 9.5. The Theory of Condensation 559
§ 9.6. Quantum Statistics of Real Gases 569
§ 9.7. The Einstein Condensation 582
§ 9.8. The λ-Transition of Helium. The Real Bose-Einstein Gas 597

Chapter X. *Molecular Distribution Functions of Real Gases* 615

§ 10.1. Direct Calculation of the Molecular Distribution Functions 615
§ 10.2. The Solution of the Born-Green Equation 626
§ 10.3. Discussion of the Born-Green Approximation 631
§ 10.4. Derivation of the Hypernetted Chain Equation and the Percus-Yevick Equation According to the Cluster Method 636
§ 10.5. Discussion of the Hypernetted Chain and the Percus-Yevick Approximations 642

Appendix

§ 1. Proof of Property 6 in § 4.4 658
§ 2. Proof of a Theorem of LEE and YANG on the Distribution of the Zeros of the Grand Partition Function of a Lattice Gas 658
§ 3. On the Kernel of the Kac Integral Equation (IV 572) 661
§ 4. Properties of the Eigenvalue Spectrum of the Kac Kernel 662
§ 5. Derivation of (IV 593) 664
§ 6. Derivation of Equation (V 117) 665
§ 7. Some Properties of the Functional Formalism 666
§ 8. Application of the Theorems of § 7 672

Index of Symbols 677

Author Index 680

Subject Index 688