

Contents

Foreword	xiii
Acknowledgments	xv
1. Introduction	3
2. Introduction to Thermodynamics	9
A. Introductory Remarks	9
B. State Variables and Exact Differentials	10
C. Equations of State	14
1. <i>Ideal Gas Law</i>	15
2. <i>Virial Expansion</i>	15
3. <i>Van der Waals Equation of State</i>	16
4. <i>Solids</i>	17
5. <i>Stretched Wire</i>	17
6. <i>Surface Tension</i>	18
7. <i>Electric Polarization</i>	18
8. <i>Curie's Law</i>	18
D. Laws of Thermodynamics	19
1. <i>Zeroth Law</i>	20
2. <i>First Law</i>	20
3. <i>Second Law</i>	21
4. <i>Third Law</i>	29
E. Fundamental Equation of Thermodynamics	31
F. Thermodynamic Potentials	32
1. <i>Internal Energy</i>	33
2. <i>Enthalpy</i>	35
3. <i>Helmholtz Free Energy</i>	37
4. <i>Gibbs Free Energy</i>	38
5. <i>Grand Potential</i>	39
6. <i>Thermodynamic Potential Densities</i>	41

G. Response Functions	41
1. <i>Heat Capacity</i>	42
2. <i>Mechanical Response Functions for PVT Systems</i>	43
3. <i>Mechanical Response Functions for Magnetic Systems</i>	44
H. Stability of the Equilibrium State	45
1. <i>Conditions for Local Equilibrium in a PVT System</i>	45
2. <i>Conditions for Local Stability</i>	47
3. <i>Implications of Stability Requirements for the Free Energies</i>	50
I. Thermodynamic Properties of a Classical Ideal Gas	52
1. <i>Internal Energy and Entropy</i>	53
2. <i>Enthalpy</i>	53
3. <i>Helmholtz and Gibbs Free Energies</i>	54
3. Applications of Thermodynamics	59
A. Introductory Remarks	59
B. Cooling and Liquefaction of Gases	60
1. <i>Joule Effect: Free Expansion</i>	60
2. <i>Joule-Thompson Effect: Throttling</i>	62
C. Entropy of Mixing and the Gibbs Paradox	66
D. Osmotic Pressure in Dilute Solutions	68
E. The Thermodynamics of Chemical Reactions	71
1. <i>The Affinity</i>	72
2. <i>Stability</i>	74
3. <i>Law of Mass Action and Heat of Reaction</i>	75
F. Thermomechanical Effect	77
4. Thermodynamics of Phase Transitions	83
A. Introductory Remarks	83
B. Coexistence of Phases: Gibbs Phase Rule	85
C. Classification of Phase Transitions	87
D. Pure PVT Systems	90
1. <i>Phase Diagrams</i>	90
2. <i>Coexistence Curves: Clausius-Clapeyron Equation</i>	92
3. <i>Liquid-Vapor Coexistence Region</i>	95
4. <i>Van der Waals Equation</i>	99
E. Regular Binary Solutions	102
F. Ginzburg-Landau Theory: λ -Points	106
G. Curie Point	109
H. Superconductors	111
1. <i>Experimental Properties</i>	111
2. <i>Ginzburg-Landau Theory of Superconductors</i>	116
I. The Helium Liquids	120
1. <i>Liquid He⁴</i>	121
2. <i>Liquid He³</i>	122
J. Critical Exponents	124

K. The Critical Exponents for Pure <i>PVT</i> Systems	126
1. <i>Experimental Values</i>	126
2. <i>Van der Waals Equation</i>	128
L. Critical Exponents for the Curie Point	130
1. <i>Degree of Critical Isotherm</i>	132
2. <i>Magnetic Exponent</i>	132
3. <i>Heat Capacity</i>	132
4. <i>Magnetic Susceptibility</i>	132
5. Elementary Probability Theory	137
A. Introductory Remarks	137
B. Permutations and Combinations	138
C. Definition of Probability	139
D. Distribution Functions	141
1. <i>Discrete Stochastic Variables</i>	141
2. <i>Continuous Stochastic Variables</i>	142
3. <i>Joint Probability Distributions</i>	144
E. Binomial Distribution	146
1. <i>Binomial Distribution</i>	146
2. <i>Gaussian (or Normal) Distribution</i>	147
3. <i>Poisson Distribution</i>	150
F. Random Walk	151
G. Central Limit Theorem	152
H. Law of Large Numbers	153
6. Master Equation	157
A. Introductory Remarks	157
B. Derivation of the Master Equation	158
C. Markov Chains	163
1. <i>Regular Transition Matrix</i>	164
2. <i>Transition Matrix with Absorbing States</i>	166
D. Random Walk and the Diffusion Equation	167
E. Discrete Stationary Markov Processes: General Solution	168
F. Birth and Death Processes	171
G. Expansion of the Master Equation	174
H. Malthus-Verhulst Equation	178
7. Probability Distributions in Dynamical Systems	185
A. Introductory Remarks	185
B. Probability Density as a Fluid	187
C. The BBGKY Hierarchy	193
D. Microscopic Balance Equations (Classical Fluids)	195
1. <i>Balance Equation for the Particle Density</i>	197
2. <i>Balance Equation for the Momentum Density</i>	197
3. <i>Balance Equation for the Energy Density</i>	199

E. Probability Density Operator	199
F. Reduced Density Operator	202
G. Wigner Function	205
H. Microscopic Balance Equations (Quantum Fluids)	209
8. Ergodic Theory	215
A. Introductory Remarks	215
B. Ergodic Flow	216
C. Mixing Flow	221
D. Anharmonic Oscillator Systems	224
9. Equilibrium Statistical Mechanics: Soluble Models	235
A. Introductory Remarks	235
B. Equilibrium Ensembles	238
1. <i>Closed Isolated Systems: Microcanonical Ensemble</i>	239
2. <i>Closed Systems: The Canonical Ensemble</i>	243
3. <i>Open Systems: Grand Canonical Ensemble</i>	246
C. Heat Capacity of Solids	249
1. <i>Classical Theory of Solids</i>	249
2. <i>Einstein Theory of Solids</i>	250
3. <i>Debye Theory of Solids</i>	252
D. Ideal Gases	256
1. <i>Classical Ideal Gas: Kinetic Theory</i>	256
2. <i>Quantum Ideal Gases: Grand Canonical Ensemble</i>	258
3. <i>Maxwell-Boltzmann Gas</i>	261
4. <i>Bose-Einstein Gas</i>	262
5. <i>Fermi-Dirac Gas</i>	267
E. Momentum Condensation in an Interacting Fermi Fluid	272
F. Order-Disorder Transitions	280
1. <i>General Discussion</i>	280
2. <i>Two Applications of the Ising Model</i>	284
3. <i>Bragg-Williams Approximation to the Ising Model</i>	285
4. <i>Exact Solution to the Ising Model</i>	289
G. The Lee-Yang Theory of Phase Transitions	292
H. Van der Waals Equation	297
1. <i>Derivation of the van der Waals Equation</i>	297
2. <i>Maxwell Construction</i>	300
10. Equilibrium Fluctuations and Critical Phenomena	307
A. Introductory Remarks	307
B. Einstein Fluctuation Theory	309
1. <i>General Discussion</i>	309
2. <i>Application to Fluid Systems</i>	311
C. Correlation Functions and Response Functions	313
1. <i>General Relations</i>	313
2. <i>Application to Fluid Systems</i>	315
3. <i>Application to Spin Systems</i>	317

D. Scaling	318
1. <i>Homogeneous Function</i>	319
2. <i>Widom Scaling</i>	320
3. <i>Kadanoff Scaling</i>	322
E. Microscopic Calculation of Critical Exponents	325
F. Critical Exponents for a Triangular Lattice	328
G. Critical Exponents for the Gaussian Model	332
H. The S^4 -Model	335
11. Classical Fluids	347
A. Introductory Remarks	347
B. Thermodynamics and the Radial Distribution Function	348
1. <i>Reduced Probability Densities</i>	348
2. <i>Thermodynamics and Reduced Probability Densities</i>	351
C. Virial Expansion of the Equation of State	355
1. <i>Virial Expansion and Cluster Functions</i>	355
2. <i>Second Virial Coefficient</i>	362
3. <i>Third Virial Coefficient</i>	367
4. <i>Higher Order Virial Coefficients</i>	371
D. Virial Expansion of the Reduced Probability Densities	373
E. Ornstein-Zernike Equation and Approximation Schemes	377
F. Superposition Principle	381
G. Experimental Results for Dense Fluids	384
H. Perturbation Theories	387
I. Quantum Corrections to the Virial Coefficients	389
1. <i>Ideal Quantum Gases</i>	390
2. <i>Interacting Quantum Gas</i>	392
12. Quantum Fluids	399
A. Introductory Remarks	399
B. Grand Potential for Normal Boson and Fermi Fluids	400
1. <i>Cumulant Expansion for the Grand Potential</i>	401
2. <i>Wick's Theorem</i>	404
3. <i>Diagrams</i>	406
C. Direct and Exchange Interactions	414
D. Electron Gas	416
1. <i>Effective Hamiltonian</i>	416
2. <i>Polarization Diagrams</i>	421
3. <i>Classical Electron Gas</i>	424
4. <i>Zero Temperature Limit</i>	426
E. Propagators for Normal Boson and Fermi Fluids	428
1. <i>Physical Interpretation</i>	428
2. <i>Diagrammatic Expansion</i>	432
F. Dyson's Equations and Self-Energy Structures	435

G. Excitations in a Weakly Coupled Fermi Fluid at Low Temperature	437
H. Weakly Coupled Condensed Boson Fluid at Zero Temperature	442
1. <i>Exact Propagator</i>	442
2. <i>Dyson's Equations</i>	446
3. <i>Chemical Potential</i>	449
4. <i>Excitations</i>	450
13. Elementary Transport Theory	455
A. Introductory Remarks	455
B. Elementary Kinetic Theory	456
1. <i>Mean Free Path</i>	457
2. <i>Collision Frequency</i>	457
3. <i>Self-Diffusion</i>	459
4. <i>Coefficients of Viscosity and Thermal Conductivity</i>	462
5. <i>Rate of Reaction</i>	465
C. The Boltzmann Equation	468
1. <i>Two-Body Scattering</i>	469
2. <i>Derivation of the Boltzmann Equation</i>	472
3. <i>Boltzmann's H-theorem</i>	473
D. Linearized Boltzmann Equations for a Two-Component System	475
E. Coefficient of Self-Diffusion	478
1. <i>Linearized Hydrodynamic Equation</i>	479
2. <i>Eigenfrequencies of the Lorentz-Boltzmann Equation</i>	480
F. Coefficients of Viscosity and Thermal Conductivity	481
1. <i>Normal Mode Frequencies of the Hydrodynamic Equations</i>	482
2. <i>Eigenfrequencies of the Boltzmann Equation</i>	488
G. Sonine Polynomials	492
H. Quantum Kinetic Equation	495
1. <i>Basic Model</i>	495
2. <i>Bogoliubov Assumption</i>	497
3. <i>Kinetic Equation</i>	499
4. <i>Spatially Homogeneous System</i>	501
14. Hydrodynamics and Onsager's Relations	507
A. Introductory Remarks	507
B. Onsager's Relations	507
1. <i>Time-Dependent Correlation Functions and Microscopic Reversibility</i>	508
2. <i>Regression of Fluctuations</i>	510
C. Onsager's Relations When a Magnetic Field Is Present	511
D. Mechanocaloric Effect and Thermomolecular Pressure Effect	514
1. <i>Mechanocaloric Effect</i>	516
2. <i>Thermomolecular Pressure Effect</i>	518

E. Minimum Entropy Production	519
F. Single-Component Normal Isotropic Fluid	523
1. <i>Conservation of Mass: Continuity Equation</i>	523
2. <i>Momentum Balance Equation</i>	523
3. <i>Energy and Entropy Balance Equations</i>	524
G. Multicomponent Fluids with Chemical Reactions	528
H. Superfluid Hydrodynamics	533
1. <i>Hydrodynamic Equations</i>	533
2. <i>First Sound</i>	537
3. <i>Second Sound</i>	538
15. Fluctuation-Dissipation Theorem	545
A. Introductory Remarks	545
B. Wiener-Khinchin Theorem	546
1. <i>Properties of Time-Dependent Correlation Matrices</i>	546
2. <i>Spectral Density Matrix</i>	547
3. <i>Spectral Density Matrix and Magnetic Fields</i>	549
C. Causality and Response Matrices	549
D. Fluctuation-Dissipation Theorem	554
E. Power Absorption	556
1. <i>Delta Function Force</i>	556
2. <i>Oscillating Force</i>	557
F. Harmonically Bound Brownian Particle	557
G. Light Scattering	560
1. <i>Phenomenology of Light Scattering</i>	561
2. <i>Intensity of Scattered Light</i>	563
3. <i>Hydrodynamic Expressions for Scattered Intensity</i>	568
H. Microscopic Linear Response Theory	571
I. Hydrodynamics and Linear Response Theory	574
J. Correlation Functions in Terms of Projection Operators	576
K. General Definition of Hydrodynamic Equations	579
1. <i>General Form of Hydrodynamic Equations</i>	579
2. <i>Hydrodynamic Modes: Conserved Quantities</i>	580
3. <i>Hydrodynamic Modes: Broken Symmetries</i>	583
L. Ferromagnetic System	587
M. Broken Symmetry in Superfluids	592
16. Long Time Tails	597
A. Introductory Remarks	597
B. Hydrodynamic Origin of the Long Time Tails	597
C. Virial Expansion of the Velocity Autocorrelation Function	602
D. Microscopic Expression for the Virial Coefficients	608
1. <i>Binary Collision Expansion</i>	609
2. <i>Ring Approximation to the Self-Energy</i>	610
3. <i>Binary Collision Operator</i>	614

E. Microscopic Derivation of the Long Time Tails	616
F. Implications for Hydrodynamics	620
17. Nonequilibrium Phase Transitions	623
A. Introductory Remarks	623
B. Thermodynamic Stability Criteria Far from Equilibrium	624
1. <i>Entropy Production</i>	624
2. <i>Nonlinear Chemical Reactions</i>	626
C. The Schlögl Model	631
D. Brusselator	633
1. <i>Real $\omega(\mathbf{k})$</i>	638
2. <i>Complex $\omega(\mathbf{k})$</i>	639
E. Lotka-Volterra Model	641
F. Bénard Instability	644
Appendices	657
A. Balance Equations	657
1. <i>General Fluid Flow</i>	657
2. <i>General Balance Equation</i>	660
B. Representations for Many-Body Quantum Systems	661
1. <i>Representations of Position and Momentum Operators</i>	662
2. <i>N-body Schrödinger Equation: General Form</i>	664
3. <i>Noninteracting Particles</i>	666
4. <i>Number Representation for Bosons</i>	669
5. <i>Number Representation for Fermions</i>	672
6. <i>Field Operators</i>	675
7. <i>Proof of Eq. (B.74)</i>	676
8. <i>Proof of Eq. (B.92)</i>	678
C. Isotropic Systems: Curie Principle	680
1. <i>Some Mathematical Properties of Tensors</i>	680
2. <i>Phenomenological Coefficients for an Isotropic System</i>	682
D. Stability of Solutions to Nonlinear Equations	683
1. <i>Linear Stability Theory</i>	683
2. <i>Limit Cycles</i>	687
3. <i>Liapounov Functions and Global Stability</i>	689
Author Index	693
Subject Index	697