

Contents

1	Introduction	1
	References	9
Part I Nonrelativistic Theories		
2	Thermodynamic Theory of Irreversible Processes	13
2.1	The Zeroth Law of Thermodynamics	14
2.1.1	The Zeroth Law of Thermodynamics for Temperature	14
2.1.2	The Zeroth Law of Thermodynamics Extended	17
2.2	The First Law of Thermodynamics	18
2.2.1	Internal Energy	19
2.2.2	Work	20
2.2.3	Local Forms of Evolution Equations	24
2.3	The Second Law of Thermodynamics	28
2.3.1	Carnot Theorem	28
2.3.2	Clausius and Kelvin Principles	29
2.3.3	Clausius Inequality	31
2.3.4	Clausius Entropy	32
2.3.5	Clausius–Duhem Inequality	36
2.4	Differential Form for Calortropy	40
2.4.1	Local Differential Form for Calortropy	41
2.4.2	Calortropy and Thermodynamic Relations	47
2.5	Generalized Hydrodynamic Equations	48
2.6	Irreversible Thermodynamics of Steady States	52
2.7	Inclusion of Chemical Reactions	54
2.8	Inclusion of Volume Transport	56
2.9	Concluding Remarks	57
	References	58

3 Boltzmann Kinetic Equation	61
3.1 Irreversible Processes in Dilute Monatomic Gases	62
3.1.1 Conserved and Nonconserved Macroscopic Variables	65
3.1.2 Collision Invariants	68
3.1.3 Broken Time Reversal Symmetry and the Boltzmann Kinetic Equation	70
3.1.4 The H Theorem and Boltzmann Entropy	72
3.2 Equilibrium Distribution Function	74
3.2.1 Equilibrium Boltzmann Entropy	75
3.2.2 Thermodynamic Correspondence and Equilibrium Gibbs Relation	76
3.3 Evolution Equations for Macroscopic Variables	78
3.3.1 Boltzmann Entropy Balance Equation	79
3.3.2 Conservation Laws of Mass, Momentum, and Energy	80
3.3.3 Evolution Equations for Nonconserved Variables	83
3.4 Thermodynamics of Irreversible Processes in Dilute Monatomic Gases	88
3.4.1 Functional Hypothesis for Distribution Functions	89
3.4.2 Calortropy and the Second Law of Thermodynamics	90
3.4.3 Thermodynamic Correspondence	97
3.5 Statistical Thermodynamics of Irreversible Processes	98
3.5.1 Nonequilibrium Intensive Properties	100
3.5.2 Nonequilibrium Partition Function	104
3.5.3 Calortropy Production in Cumulant Expansion	110
3.5.4 Cumulant Expansion for Dissipation Terms	113
3.5.5 Collision Bracket Integrals	114
3.5.6 Generalized Potentials	115
3.5.7 Quasilinear Generalized Hydrodynamics and Transport Processes	117
3.5.8 Linear Transport Processes	119
3.5.9 A Model for Quasilinear Generalized Hydrodynamic Equations	121
3.6 Relative Boltzmann Entropy	121
3.6.1 Evolution Equation of Relative Boltzmann Entropy	122
3.6.2 Relative Boltzmann Entropy and Fluctuations	124
3.6.3 Differential Equations for Fluctuations	126
3.6.4 Stochastic Treatment of Fluctuations	129
3.7 Concluding Remarks	135
References	135

4 Equilibrium Ensemble Method	137
4.1 Brief Review of Ensemble Methods	137
4.2 Ensembles and Fundamental Postulates	138
4.2.1 Canonical Ensemble	141
4.2.2 Grand Canonical Ensemble	148
4.3 Summary of the Gibbs Ensemble Theory	154
References	154
5 Boltzmann-Like Equation for Moderately Dense Gases	157
5.1 Extended Boltzmann Equation	158
5.2 Cluster Expansion of the N -Particle Collision Operator	173
5.3 Macroscopic Evolution Equations	177
5.3.1 Boltzmann Entropy, Calortropy, and Relative Boltzmann Entropy	178
5.3.2 Conservation Laws	180
5.3.3 Nonconserved Variables and Their Evolution Equations	181
5.4 Equilibrium Solution of the Extended Boltzmann Kinetic Equation	183
5.5 Thermodynamics of Irreversible Processes and Hydrodynamics	184
5.5.1 Nonequilibrium Canonical Distribution Functions	185
5.5.2 Calortropy Differential	186
5.5.3 Thermodynamic Correspondence	188
5.5.4 Nonequilibrium Statistical Thermodynamics of Irreversible Processes	189
5.5.5 Generalized Potentials	190
5.5.6 Calortropy Production in Cumulant Expansion	191
5.5.7 Cumulant Expansion for Dissipation Terms	195
5.5.8 Quasilinear Generalized Hydrodynamic Equations	196
5.5.9 Collision Bracket Integrals	198
5.5.10 Steady Quasilinear and Linear Transport Processes	199
5.5.11 A Model for Quasilinear Generalized Hydrodynamic Equations	206
5.5.12 Density Expansion of Extended Boltzmann Collision Integral	207
5.6 Concluding Remarks	211
References	212
6 Kinetic Theory of a Simple Dense Fluid	213
6.1 Generalized Boltzmann Equation	214
6.2 Basic Properties of the Generalized Boltzmann Equation	227
6.2.1 Collision Invariants	228
6.2.2 The H Theorem and the Stability Condition	229
6.2.3 Proof of Conditions (6.C1) and (6.C2)	229

6.3	Conservation Laws	232
6.3.1	Mass Conservation Law	232
6.3.2	Momentum Conservation Law	233
6.3.3	Energy Conservation Law	236
6.4	Voronoi Volume—a Concept of Molar Volume	237
6.5	Evolution Equation of Volume Fluctuations	244
6.6	Evolution Equations for Other Nonconserved Variables	247
6.6.1	Evolution Equation of Volume Flux	249
6.6.2	Shear Stress Evolution Equation	250
6.6.3	Evolution Equation for Excess Normal Stress	252
6.6.4	Evolution Equation for Heat Flux	254
6.7	Thermodynamics of Irreversible Processes	258
6.7.1	Boltzmann Entropy	258
6.7.2	Calortropy	261
6.7.3	Relative Boltzmann Entropy	263
6.7.4	Equilibrium Solution of the GBE	264
6.7.5	Nonequilibrium Canonical Form for the Distribution Function	268
6.7.6	Calortropy and Its Differential Form	270
6.7.7	Thermodynamic Correspondence	274
6.7.8	Local Form of the Second Law of Thermodynamics	275
6.7.9	Nonequilibrium Partition Function	278
6.7.10	Nonequilibrium Statistical Thermodynamics	279
6.7.11	Determination of Generalized Potentials	280
6.7.12	Cumulant Expansion for Dissipation Terms	281
6.7.13	Collision Bracket Integrals	286
6.7.14	Summary of Generalized Hydrodynamic Equations	289
6.8	Linear Constitutive Equations for Nonconserved Moments	290
6.8.1	Constitutive Equation for Volume Fluctuation $\Phi^{(0)}$	291
6.8.2	Constitutive Equation for Shear Stress $\Phi^{(1)}$	292
6.8.3	Constitutive Relation for Excess Normal Stress $\Phi^{(2)}$	293
6.8.4	Constitutive Relation for Heat Flux $\Phi^{(3)}$	293
6.8.5	Constitutive Relation for Volume Flux $\Phi^{(4)}$	294
6.8.6	Linear Transport Coefficients	294
6.9	Quasilinear Generalized Hydrodynamic Equations	297
6.10	Model for Quasilinear Generalized Hydrodynamic Equations	297
6.11	Relative Boltzmann Entropy Revisited	301
6.11.1	Exponential Form for $\bar{f}^{(N)}$	301
6.11.2	Relative Boltzmann Entropy Balance Equation	303

6.11.3	Stochastic Theory Approach to the Generalized Boltzmann Equation	306
6.12	Barycentric Velocity and Its Constitutive Equation	308
6.12.1	Cartesian Coordinate Representation	308
6.12.2	Transformation to Collective Coordinates	313
6.13	Brownian Motion Model	315
6.14	Concluding Remarks	317
	References	318
7	Kinetic Theory of a Dense Simple Fluid Mixture	321
7.1	Generalized Boltzmann Equation for a Simple Fluid Mixture	322
7.1.1	Nonequilibrium Grand Ensemble	322
7.1.2	Generalized Boltzmann Equation for a Mixture	324
7.2	Boltzmann Entropy and the H Theorem	331
7.2.1	Boltzmann Entropy	332
7.2.2	Boltzmann Entropy Balance Equation	333
7.2.3	Equilibrium Distribution Function	335
7.3	Conserved Variables	337
7.4	Nonconserved Variables and Their Evolution Equations	341
7.4.1	Generic Form of Evolution Equations	342
7.4.2	Physically Most Relevant Nonconserved Moments	344
7.5	Set of Macroscopic Moments	347
7.5.1	Conserved Moments	348
7.5.2	Nonconserved Moments	353
7.6	Generalized Hydrodynamic Equations	365
7.6.1	Conservation Laws	366
7.6.2	Evolution Equations for Nonconserved Variables	372
7.7	Thermodynamics of Irreversible Processes in a Mixture	386
7.7.1	Nonequilibrium Grand Canonical Ensemble Theory	387
7.7.2	Calortropy	388
7.7.3	Thermodynamic Correspondence	393
7.7.4	Nonequilibrium Statistical Thermodynamics	394
7.7.5	Local and Global Representation of Thermodynamic Laws	396
7.7.6	Generalized Potentials	399
7.7.7	Cumulant Expansion for Calortropy Production and Dissipation Terms	401
7.7.8	Collision Bracket Integrals	405
7.8	Linear Transport Processes	408
7.8.1	Linear Dissipation Terms	408
7.8.2	Linear Constitutive Equations	409
7.8.3	Linear Transport Coefficients	416

7.9	Summary of Generalized Hydrodynamic Equations for a Mixture	418
7.9.1	Conservation Laws	419
7.9.2	Nonconserved Evolution Equations	419
7.10	Quasilinear Generalized Hydrodynamic Equations	420
7.11	Relative Boltzmann Entropy	423
7.12	Concluding Remarks	427
	References	428
8	Classical Scattering Theory in Phase Space	429
8.1	Preamble to Classical Scattering Theory	430
8.2	Eigenvalue Problem for the Classical Liouville Operator	431
8.3	Some Mathematical Properties of Eigenfunctions and Eigenvalues	437
8.4	Formal Scattering Theory in Phase Space	442
8.5	Alternative Form for the Collision Bracket Integral	447
8.5.1	Example for Two-Particle Collisions	451
8.5.2	Three-Particle Collision	452
8.6	Application of the Computational Algorithm	453
8.6.1	Linear Transport Coefficients for a Moderately Dense Gas Mixture	453
8.6.2	Shear Viscosity	456
8.6.3	Bulk Viscosity	457
8.6.4	Thermal Conductivity, Thermal Diffusion, and Mass Diffusion	458
8.7	Concluding Remarks	460
	References	461
9	Generalized Hydrodynamics and Transport Processes	463
9.1	Generalized Hydrodynamics for Dilute Gases	464
9.1.1	Conservation Laws	465
9.1.2	Evolution Equations for Nonconserved Variables	466
9.1.3	Reduced Generalized Hydrodynamic Equations for Gases	472
9.1.4	Quasilinear Transport Phenomena	479
9.1.5	Dissipation Function and Thermodynamic Forces	482
9.1.6	Nonlinear Transport Coefficients	485
9.1.7	Linear Transport Coefficients and Classical Hydrodynamics	487
9.1.8	Quasilinear Transport Processes and Hyperbolic-Type Partial Differential Equations	488
9.2	Applications of Generalized Hydrodynamic Equations for Gases	495
9.2.1	Compressible Poiseuille Gas Flow	496
9.2.2	Integration of Conservation Laws	498

9.2.3	Reduction of Constitutive Relations to an Independent Set	498
9.2.4	Rarefied Gas Flow Past a Circular Cylinder	502
9.2.5	The Knudsen Problem	504
9.2.6	Light-Induced Gas Flow in Rarefied Gas	510
9.3	Generalized Hydrodynamics for Liquids	516
9.3.1	Quasilinear Generalized Hydrodynamics and Transport Processes	516
9.3.2	Balance Equations for Conserved Variables	516
9.3.3	Quasilinear Nonconserved Evolution Equations	516
9.3.4	Volume Transport Phenomena	519
9.3.5	Shear Viscous Transport	520
9.3.6	Heat Conduction, Diffusion, Volume Flux	521
9.3.7	Quasilinear and Linear Transport Coefficients	524
9.4	Concluding Remarks	527
	References	528

Epilogue: Non-Relativistic Theories

Part II Essays on Equilibrium Theories

10	Molecular Theory of Liquid Mixtures: Equilibrium Properties . . .	537
10.1	Kirkwood–Buff Theory of Mixtures	538
10.1.1	Chemical Potentials	542
10.1.2	Partial Molar Volumes and Isothermal Compressibility	543
10.1.3	Equation of State	545
10.1.4	Chemical Potentials Revisited	545
10.1.5	Osmotic Pressure	548
10.2	Ornstein–Zernike Theory of Solutions	550
10.3	The KB Theory Recast	551
10.3.1	Partial Molar Volumes and Isothermal Compressibility	552
10.3.2	Chemical Potentials Recast	554
10.3.3	Osmotic Pressure Recast	556
10.3.4	Entropy of Mixing	558
10.3.5	Enthalpy of Mixtures	559
10.4	Monte Carlo Simulation Method for Pair Correlation Functions	559
	References	560
11	Equilibrium Pair Correlation Functions	561
11.1	Integral Equation Method for Pair Correlation Functions	561
11.1.1	The Wiener–Hopf Method of Solution for the OZ Equation	563

11.1.2	Integral Equation for the Direct Correlation Function	566
11.1.3	Integral Equation for the Total Correlation Function	568
11.1.4	Thermodynamically Consistent Closure.	570
11.1.5	Function $\Psi(\mathbf{x})$	572
11.1.6	Equation for Inverse Correlation Length	575
11.2	Pair Correlation Function in the Subcritical Regime	575
11.3	Concluding Remarks	581
	References	582
Appendix A: List of Symbols (Volume 1)		585
Index		593