

Contents

Preface to the Fourth Edition *XIII*

1	Introduction	1
2	Complexity and Entropy	5
2.1	Introduction	5
2.2	Counting Microscopic States	5
2.3	Probability	9
2.4	Multiplicity and Entropy of Macroscopic Physical States	11
2.5	Multiplicity and Entropy of a Spin System	12
2.5.1	Multiplicity of a Spin System	12
2.5.2	Entropy of Spin System	13
2.6	Entropic Tension in a Polymer	16
2.7	Multiplicity and Entropy of an Einstein Solid	18
2.7.1	Multiplicity of an Einstein Solid	18
2.7.2	Entropy of the Einstein Solid	19
2.8	Multiplicity and Entropy of an Ideal Gas	20
2.8.1	Multiplicity of an Ideal Gas	20
2.8.2	Entropy of an Ideal Gas	22
2.9	Problems	23
3	Thermodynamics	27
3.1	Introduction	27
3.2	Energy Conservation	29
3.3	Entropy	30
3.3.1	Carnot Engine	30
3.3.2	The Third Law	34
3.4	Fundamental Equation of Thermodynamics	35
3.5	Thermodynamic Potentials	38
3.5.1	Internal Energy	39
3.5.2	Enthalpy	40
3.5.3	Helmholtz Free Energy	42
3.5.4	Gibbs Free Energy	43

3.5.5	Grand Potential	45
3.6	Response Functions	46
3.6.1	Thermal Response Functions (Heat Capacity)	46
3.6.2	Mechanical Response Functions	49
3.7	Stability of the Equilibrium State	51
3.7.1	Conditions for Local Equilibrium in a PVT System	51
3.7.2	Conditions for Local Stability in a PVT System	52
3.7.3	Implications of the Stability Requirements for the Free Energies	56
3.7.4	Correlations Between Fluctuations	58
3.8	Cooling and Liquefaction of Gases	61
3.9	Osmotic Pressure in Dilute Solutions	64
3.10	The Thermodynamics of Chemical Reactions	67
3.10.1	The Affinity	68
3.11	The Thermodynamics of Electrolytes	74
3.11.1	Batteries and the Nernst Equation	75
3.11.2	Cell Potentials and the Nernst Equation	77
3.12	Problems	78
4	The Thermodynamics of Phase Transitions	87
4.1	Introduction	87
4.2	Coexistence of Phases: Gibbs Phase Rule	88
4.3	Classification of Phase Transitions	89
4.4	Classical Pure PVT Systems	91
4.4.1	Phase Diagrams	91
4.4.2	Coexistence Curves: Clausius–Clapeyron Equation	92
4.4.3	Liquid–Vapor Coexistence Region	95
4.4.4	The van der Waals Equation	100
4.4.5	Steam Engines – The Rankine Cycle	102
4.5	Binary Mixtures	105
4.5.1	Equilibrium Conditions	106
4.6	The Helium Liquids	108
4.6.1	Liquid He^4	109
4.6.2	Liquid He^3	112
4.6.3	Liquid He^3 - He^4 Mixtures	113
4.7	Superconductors	114
4.8	Ginzburg–Landau Theory	116
4.8.1	Continuous Phase Transitions	117
4.8.2	First-Order Transitions	120
4.8.3	Some Applications of Ginzburg–Landau Theory	121
4.9	Critical Exponents	123
4.9.1	Definition of Critical Exponents	124
4.9.2	The Critical Exponents for Pure PVT Systems	124
4.9.3	The Critical Exponents for the Curie Point	126
4.9.4	The Critical Exponents for Mean Field Theories	128
4.10	Problems	130

5	Equilibrium Statistical Mechanics I – Canonical Ensemble	135
5.1	Introduction	135
5.2	Probability Density Operator – Canonical Ensemble	137
5.2.1	Energy Fluctuations	138
5.3	Semiclassical Ideal Gas of Indistinguishable Particles	139
5.3.1	Approximations to the Partition Function for Semiclassical Ideal Gases	139
5.3.2	Maxwell–Boltzmann Distribution	143
5.4	Interacting Classical Fluids	145
5.4.1	Density Correlations and the Radial Distribution Function	146
5.4.2	Magnetization Density Correlations	148
5.5	Heat Capacity of a Debye Solid	149
5.6	Order–Disorder Transitions on Spin Lattices	153
5.6.1	Exact Solution for a One-Dimensional Lattice	154
5.6.2	Mean Field Theory for a d -Dimensional Lattice	156
5.6.3	Mean Field Theory of Spatial Correlation Functions	159
5.6.4	Exact Solution to Ising Lattice for $d = 2$	160
5.7	Scaling	162
5.7.1	Homogeneous Functions	162
5.7.2	Widom Scaling	163
5.7.3	Kadanoff Scaling	166
5.8	Microscopic Calculation of Critical Exponents	169
5.8.1	General Theory	169
5.8.2	Application to Triangular Lattice	172
5.8.3	The S^4 Model	175
5.9	Problems	177
6	Equilibrium Statistical Mechanics II – Grand Canonical Ensemble	183
6.1	Introduction	183
6.2	The Grand Canonical Ensemble	184
6.2.1	Particle Number Fluctuations	185
6.2.2	Ideal Classical Gas	186
6.3	Adsorption Isotherms	187
6.4	Virial Expansion for Interacting Classical Fluids	191
6.4.1	Virial Expansion and Cluster Functions	191
6.4.2	The Second Virial Coefficient, $B_2(T)$	194
6.5	Blackbody Radiation	197
6.6	Ideal Quantum Gases	200
6.7	Ideal Bose–Einstein Gas	202
6.7.1	Bose–Einstein Condensation	206
6.7.2	Experimental Observation of Bose–Einstein Condensation	208
6.8	Bogoliubov Mean Field Theory	210
6.9	Ideal Fermi–Dirac Gas	214
6.10	Magnetic Susceptibility of an Ideal Fermi Gas	220
6.10.1	Paramagnetism	221

6.10.2	Diamagnetism	222
6.11	Momentum Condensation in an Interacting Fermi Fluid	224
6.12	Problems	231
7	Brownian Motion and Fluctuation–Dissipation	235
7.1	Introduction	235
7.2	Brownian Motion	236
7.2.1	Langevin Equation	237
7.2.2	Correlation Function and Spectral Density	238
7.3	The Fokker–Planck Equation	240
7.3.1	Probability Flow in Phase Space	242
7.3.2	Probability Flow for Brownian Particle	243
7.3.3	The Strong Friction Limit	245
7.4	Dynamic Equilibrium Fluctuations	250
7.4.1	Regression of Fluctuations	252
7.4.2	Wiener–Khinchine Theorem	253
7.5	Linear Response Theory and the Fluctuation–Dissipation Theorem	255
7.5.1	The Response Matrix	255
7.5.2	Causality	257
7.5.3	The Fluctuation–Dissipation Theorem	260
7.5.4	Power Absorption	262
7.6	Microscopic Linear Response Theory	264
7.6.1	Density Operator Perturbed by External Field	264
7.6.2	The Electric Conductance	265
7.6.3	Power Absorption	270
7.7	Thermal Noise in the Electron Current	272
7.8	Problems	273
8	Hydrodynamics	277
8.1	Introduction	277
8.2	Navier–Stokes Hydrodynamic Equations	278
8.2.1	Balance Equations	278
8.2.2	Entropy Source and Entropy Current	283
8.2.3	Transport Coefficients	286
8.3	Linearized Hydrodynamic Equations	289
8.3.1	Linearization of the Hydrodynamic Equations	289
8.3.2	Transverse Hydrodynamic Modes	293
8.3.3	Longitudinal Hydrodynamic Modes	294
8.3.4	Dynamic Correlation Function and Spectral Density	296
8.4	Light Scattering	297
8.4.1	Scattered Electric Field	299
8.4.2	Intensity of Scattered Light	301
8.5	Friction on a Brownian particle	303
8.6	Brownian Motion with Memory	307

8.7	Hydrodynamics of Binary Mixtures	311
8.7.1	Entropy Production in Binary Mixtures	312
8.7.2	Fick's Law for Diffusion	315
8.7.3	Thermal Diffusion	317
8.8	Thermoelectricity	318
8.8.1	The Peltier Effect	318
8.8.2	The Seebeck Effect	320
8.8.3	Thomson Heat	321
8.9	Superfluid Hydrodynamics	322
8.9.1	Superfluid Hydrodynamic Equations	322
8.9.2	Sound Modes	326
8.10	Problems	329
9	Transport Coefficients	333
9.1	Introduction	333
9.2	Elementary Transport Theory	334
9.2.1	Transport of Molecular Properties	338
9.2.2	The Rate of Reaction	339
9.3	The Boltzmann Equation	341
9.3.1	Derivation of the Boltzmann Equation	342
9.4	Linearized Boltzmann Equations for Mixtures	343
9.4.1	Kinetic Equations for a Two-Component Gas	344
9.4.2	Collision Operators	346
9.5	Coefficient of Self-Diffusion	348
9.5.1	Derivation of the Diffusion Equation	348
9.5.2	Eigenfrequencies of the Lorentz–Boltzmann Equation	349
9.6	Coefficients of Viscosity and Thermal Conductivity	351
9.6.1	Derivation of the Hydrodynamic Equations	351
9.6.2	Eigenfrequencies of the Boltzmann Equation	355
9.6.3	Shear Viscosity and Thermal Conductivity	358
9.7	Computation of Transport Coefficients	359
9.7.1	Sonine Polynomials	359
9.7.2	Diffusion Coefficient	360
9.7.3	Thermal Conductivity	361
9.7.4	Shear Viscosity	363
9.8	Beyond the Boltzmann Equation	365
9.9	Problems	366
10	Nonequilibrium Phase Transitions	369
10.1	Introduction	369
10.2	Near Equilibrium Stability Criteria	370
10.3	The Chemically Reacting Systems	372
10.3.1	The Brusselator – A Nonlinear Chemical Model	373
10.3.2	Boundary Conditions	374
10.3.3	Stability Analysis	375

10.3.4	Chemical Crystals	377
10.4	The Rayleigh–Bénard Instability	378
10.4.1	Hydrodynamic Equations and Boundary Conditions	379
10.4.2	Linear Stability Analysis	382
10.5	Problems	385

Appendix A Probability and Stochastic Processes 387

A.1	Probability	387
A.1.1	Definition of Probability	387
A.1.2	Probability Distribution Functions	389
A.1.3	Binomial Distributions	393
A.1.4	Central Limit Theorem and the Law of Large Numbers	400
A.2	Stochastic Processes	402
A.2.1	Markov Chains	402
A.2.2	The Master Equation	405
A.2.3	Probability Density for Classical Phase Space	409
A.2.4	Quantum Probability Density Operator	412
A.3	Problems	415

Appendix B Exact Differentials 417

Appendix C Ergodicity 421

Appendix D Number Representation 425

D.1	Symmetrized and Antisymmetrized States	425
D.1.1	Free Particles	426
D.1.2	Particle in a Box	426
D.1.3	N -Particle Eigenstates	427
D.1.4	Symmetrized Momentum Eigenstates for Bose–Einstein Particles	427
D.1.5	Antisymmetrized Momentum Eigenstates for Fermi–Dirac Particles	428
D.1.6	Partition Functions and Expectation Values	429
D.2	The Number Representation	431
D.2.1	The Number Representation for Bosons	431
D.2.2	The Number Representation for Fermions	434
D.2.3	Thermodynamic Averages of Quantum Operators	435

Appendix E Scattering Theory 437

E.1	Classical Dynamics of the Scattering Process	437
E.2	The Scattering Cross Section	440
E.3	Quantum Dynamics of Low-Energy Scattering	442

	Appendix F Useful Math and Problem Solutions	445
F.1	Useful Mathematics	445
F.2	Solutions for Odd-Numbered Problems	447
	References	453
	Index	459