

Contents^A

<i>Preface</i>	xiii
1. Disorder or Uncertainty?	1
2. Classical Thermodynamics	5
2.1 The Classical Laws of Thermodynamics	5
2.2 Macroscopic State Variables and Thermodynamic Processes	6
2.3 Properties of the Ideal Classical Gas	8
2.4 Thermodynamic Processing of the Ideal Gas	10
2.5 Entropy of the Ideal Gas	13
2.6 Entropy Change in Free Expansion of an Ideal Gas	15
2.7 Entropy Change due to Nonquasistatic Heat Transfer	17
2.8 Cyclic Thermodynamic Processes, the Clausius Inequality and Carnot's Theorem	19
2.9 Generality of the Clausius Expression for Entropy Change	21
2.10 Entropy Change due to Nonquasistatic Work	23
2.11 Fundamental Relation of Thermodynamics	25
2.12 Entropy Change due to Nonquasistatic Particle Transfer	28
2.13 Entropy Change due to Nonquasistatic Volume Exchange	30
2.14 General Thermodynamic Driving	31
2.15 Reversible and Irreversible Processes	32
2.16 Statements of the Second Law	33
2.17 Classical Thermodynamics: the Salient Points	35
Exercises	35
3. Applications of Classical Thermodynamics	37
3.1 Fluid Flow and Throttling Processes	37
3.2 Thermodynamic Potentials and Availability	39
3.2.1 Helmholtz Free Energy	40
3.2.2 Why <i>Free</i> Energy?	43
3.2.3 Contrast between Equilibria	43
3.2.4 Gibbs Free Energy	44
3.2.5 Grand Potential	46
3.3 Maxwell Relations	47
3.4 Nonideal Classical Gas	48
3.5 Relationship between Heat Capacities	49

3.6	General Expression for an Adiat	50
3.7	Determination of Entropy from a Heat Capacity	50
3.8	Determination of Entropy from an Equation of State	51
3.9	Phase Transitions and Phase Diagrams	52
3.9.1	Conditions for Coexistence	53
3.9.2	Clausius–Clapeyron Equation	55
3.9.3	The Maxwell Equal Areas Construction	57
3.9.4	Metastability and Nucleation	59
3.10	Work Processes without Volume Change	59
3.11	Consequences of the Third Law	60
3.12	Limitations of Classical Thermodynamics	61
	Exercises	62
4.	Core Ideas of Statistical Thermodynamics	65
4.1	The Nature of Probability	65
4.2	Dynamics of Complex Systems	68
4.2.1	The Principle of Equal a Priori Probabilities	68
4.2.2	Microstate Enumeration	71
4.3	Microstates and Macrostates	72
4.4	Boltzmann’s Principle and the Second Law	75
4.5	Statistical Ensembles	77
4.6	Statistical Thermodynamics: the Salient Points	78
	Exercises	79
5.	Statistical Thermodynamics of a System of Harmonic Oscillators	81
5.1	Microstate Enumeration	81
5.2	Microcanonical Ensemble	83
5.3	Canonical Ensemble	84
5.4	The Thermodynamic Limit	88
5.5	Temperature and the Zeroth Law of Thermodynamics	91
5.6	Generalisation	91
	Exercises	92
6.	The Boltzmann Factor and the Canonical Partition Function	95
6.1	Simple Applications of the Boltzmann Factor	95
6.1.1	Maxwell–Boltzmann Distribution	95
6.1.2	Single Classical Oscillator and the Equipartition Theorem	97
6.1.3	Isothermal Atmosphere Model	98
6.1.4	Escape Problems and Reaction Rates	99
6.2	Mathematical Properties of the Canonical Partition Function	99
6.3	Two-Level Paramagnet	101
6.4	Single Quantum Oscillator	103
6.5	Heat Capacity of a Diatomic Molecular Gas	104
6.6	Einstein Model of the Heat Capacity of Solids	105
6.7	Vacancies in Crystals	106
	Exercises	108

7. The Grand Canonical Ensemble and Grand Partition Function	111
7.1 System of Harmonic Oscillators	111
7.2 Grand Canonical Ensemble for a General System	115
7.3 Vacancies in Crystals Revisited	116
Exercises	117
8. Statistical Models of Entropy	119
8.1 Boltzmann Entropy	119
8.1.1 The Second Law of Thermodynamics	120
8.1.2 The Maximum Entropy Macrostate of Oscillator Spikiness	122
8.1.3 The Maximum Entropy Macrostate of Oscillator Populations	122
8.1.4 The Third Law of Thermodynamics	126
8.2 Gibbs Entropy	127
8.2.1 Fundamental Relation of Thermodynamics and Thermodynamic Work	129
8.2.2 Relationship to Boltzmann Entropy	130
8.2.3 Third Law Revisited	131
8.3 Shannon Entropy	131
8.4 Fine and Coarse Grained Entropy	132
8.5 Entropy at the Nanoscale	133
8.6 Disorder and Uncertainty	134
Exercises	135
9. Statistical Thermodynamics of the Classical Ideal Gas	137
9.1 Quantum Mechanics of a Particle in a Box	137
9.2 Densities of States	138
9.3 Partition Function of a One-Particle Gas	140
9.4 Distinguishable and Indistinguishable Particles	141
9.5 Partition Function of an N -Particle Gas	145
9.6 Thermal Properties and Consistency with Classical Thermodynamics	146
9.7 Condition for Classical Behaviour	147
Exercises	149
10. Quantum Gases	151
10.1 Spin and Wavefunction Symmetry	151
10.2 Pauli Exclusion Principle	152
10.3 Phenomenology of Quantum Gases	153
Exercises	154
11. Boson Gas	155
11.1 Grand Partition Function for Bosons in a Single Particle State	155
11.2 Bose–Einstein Statistics	156
11.3 Thermal Properties of a Boson Gas	158
11.4 Bose–Einstein Condensation	161
11.5 Cooper Pairs and Superconductivity	166
Exercises	167

12. Fermion Gas	169
12.1 Grand Partition Function for Fermions in a Single Particle State	169
12.2 Fermi–Dirac Statistics	170
12.3 Thermal Properties of a Fermion Gas	171
12.4 Maxwell–Boltzmann Statistics	173
12.5 The Degenerate Fermion Gas	176
12.6 Electron Gas in Metals	177
12.7 White Dwarfs and the Chandrasekhar Limit	179
12.8 Neutron Stars	182
12.9 Entropy of a Black Hole	183
Exercises	184
13. Photon Gas	187
13.1 Electromagnetic Waves in a Box	187
13.2 Partition Function of the Electromagnetic Field	189
13.3 Thermal Properties of a Photon Gas	191
13.3.1 Planck Energy Spectrum of Black-Body Radiation	191
13.3.2 Photon Energy Density and Flux	193
13.3.3 Photon Pressure	193
13.3.4 Photon Entropy	194
13.4 The Global Radiation Budget and Climate Change	195
13.5 Cosmic Background Radiation	197
Exercises	198
14. Statistical Thermodynamics of Interacting Particles	201
14.1 Classical Phase Space	201
14.2 Virial Expansion	203
14.3 Harmonic Structures	206
14.3.1 Triatomic Molecule	207
14.3.2 Einstein Solid	208
14.3.3 Debye Solid	209
Exercises	211
15. Thermodynamics away from Equilibrium	213
15.1 Nonequilibrium Classical Thermodynamics	213
15.1.1 Energy and Particle Currents and their Conjugate Thermodynamic Driving Forces	213
15.1.2 Entropy Production in Constrained and Evolving Systems	218
15.2 Nonequilibrium Statistical Thermodynamics	220
15.2.1 Probability Flow and the Principle of Equal a Priori Probabilities	220
15.2.2 The Dynamical Basis of the Principle of Entropy Maximisation	222
Exercises	223
16. The Dynamics of Probability	225
16.1 The Discrete Random Walk	225

16.2	Master Equations	226
16.2.1	Solution to the Random Walk	228
16.2.2	Entropy Production during a Random Walk	229
16.3	The Continuous Random Walk and the Fokker–Planck Equation	230
16.3.1	Wiener Process	232
16.3.2	Entropy Production in the Wiener Process	233
16.4	Brownian Motion	235
16.5	Transition Probability Density for a Harmonic Oscillator	236
	Exercises	238
17.	Fluctuation Relations	241
17.1	Forward and Backward Path Probabilities: a Criterion for Equilibrium	241
17.2	Time Asymmetry of Behaviour and a Definition of Entropy Production	243
17.3	The Relaxing Harmonic Oscillator	245
17.4	Entropy Production Arising from a Single Random Walk	247
17.5	Further Fluctuation Relations	249
17.6	The Fundamental Basis of the Second Law	253
	Exercises	253
18.	Final Remarks	255
	<i>Further Reading</i>	261
	<i>Index</i>	263