

# Contents

<b>Preface</b>	xv
<b>1 Introduction</b>	1
1.1 Thermal Physics	1
1.2 What are the Questions?	2
1.3 History	2
1.4 Basic Concepts and Assumptions	4
1.5 Road Map	5
<b>Part I Entropy</b>	
<b>2 The Classical Ideal Gas</b>	11
2.1 Ideal Gas	11
2.2 Phase Space of a Classical Gas	12
2.3 Distinguishability	12
2.4 Probability Theory	13
2.5 Boltzmann's Definition of the Entropy	13
2.6 $S = k \log W$	14
2.7 Independence of Positions and Momenta	14
2.8 Road Map for Part I	15
<b>3 Discrete Probability Theory</b>	16
3.1 What is Probability?	16
3.2 Discrete Random Variables and Probabilities	17
3.3 Probability Theory for Multiple Random Variables	18
3.4 Random Numbers and Functions of Random Variables	20
3.5 Mean, Variance, and Standard Deviation	22
3.6 Correlation Functions	23
3.7 Sets of Independent Random Numbers	24
3.8 Binomial Distribution	25
3.9 Gaussian Approximation to the Binomial Distribution	27
3.10 A Digression on Gaussian Integrals	28
3.11 Stirling's Approximation for $N!$	29
3.12 Binomial Distribution with Stirling's Approximation	32
3.13 Problems	33
<b>4 The Classical Ideal Gas: Configurational Entropy</b>	40
4.1 Separation of Entropy into Two Parts	40
4.2 Distribution of Particles between Two Subsystems	41
4.3 Consequences of the Binomial Distribution	42
4.4 Actual Number versus Average Number	43



14.3	First and Second Derivatives	139	18	<b>The Nernst Postulate: the Third Law of Thermodynamics</b>	194
14.4	Standard Set of Second Derivatives	140	18.1	Classical Ideal Gas Violates the Nernst Postulate	194
14.5	Maxwell Relations	141	18.2	Planck's Form of the Nernst Postulate	195
14.6	Manipulating Partial Derivatives	143	18.3	Consequences of the Nernst Postulate	195
14.7	Working with Jacobians	146	18.4	Coefficient of Thermal Expansion at Low Temperatures	196
14.8	Examples of Identity Derivations	148	18.5	Summary and Signposts	197
14.9	General Strategy	151			
14.10	Problems	152		Part III Classical Statistical Mechanics	
<b>15</b>	<b>Extremum Principles</b>	156	<b>19</b>	<b>Ensembles in Classical Statistical Mechanics</b>	201
15.1	Energy Minimum Principle	156	19.1	Microcanonical Ensemble	202
15.2	Minimum Principle for the Helmholtz Free Energy	159	19.2	Molecular Dynamics: Computer Simulations	202
15.3	Minimum Principle for the Enthalpy	162	19.3	Canonical Ensemble	204
15.4	Minimum Principle for the Gibbs Free Energy	163	19.4	The Partition Function as an Integral over Phase Space	207
15.5	Exergy	164	19.5	The Liouville Theorem	207
15.6	Maximum Principle for Massieu Functions	165	19.6	Consequences of the Canonical Distribution	209
15.7	Summary	165	19.7	The Helmholtz Free Energy	210
15.8	Problems	165	19.8	Thermodynamic Identities	211
<b>16</b>	<b>Stability Conditions</b>	167	19.9	Beyond Thermodynamic Identities	212
16.1	Intrinsic Stability	167	19.10	Integration over the Momenta	213
16.2	Stability Criteria based on the Energy Minimum Principle	168	19.11	Monte Carlo Computer Simulations	214
16.3	Stability Criteria based on the Helmholtz Free Energy Minimum Principle	170	19.12	Factorization of the Partition Function: the Best Trick in Statistical Mechanics	217
16.4	Stability Criteria based on the Enthalpy Minimization Principle	171	19.13	Simple Harmonic Oscillator	218
16.5	Inequalities for Compressibilities and Specific Heats	172	19.14	Problems	220
16.6	Other Stability Criteria	173	<b>20</b>	<b>Classical Ensembles: Grand and Otherwise</b>	227
16.7	Problems	175	20.1	Grand Canonical Ensemble	227
<b>17</b>	<b>Phase Transitions</b>	177	20.2	Grand Canonical Probability Distribution	228
17.1	The van der Waals Fluid	178	20.3	Importance of the Grand Canonical Partition Function	230
17.2	Derivation of the van der Waals Equation	178	20.4	$\mathcal{Z}(T, V, \mu)$ for the Ideal Gas	231
17.3	Behavior of the van der Waals Fluid	179	20.5	Summary of the Most Important Ensembles	231
17.4	Instabilities	180	20.6	Other Classical Ensembles	232
17.5	The Liquid–Gas Phase Transition	182	20.7	Problems	232
17.6	Maxwell Construction	184	<b>21</b>	<b>Irreversibility</b>	234
17.7	Coexistent Phases	184	21.1	What Needs to be Explained?	234
17.8	Phase Diagram	185	21.2	Trivial Form of Irreversibility	235
17.9	Helmholtz Free Energy	186	21.3	Boltzmann's H-Theorem	235
17.10	Latent Heat	188	21.4	Loschmidt's <i>Umkehrwand</i>	235
17.11	The Clausius–Clapeyron Equation	188	21.5	Zermelo's <i>Wiederkehrwand</i>	236
17.12	Gibbs' Phase Rule	190	21.6	Free Expansion of a Classical Ideal Gas	236
17.13	Problems	191	21.7	Zermelo's <i>Wiederkehrwand</i> Revisited	240
			21.8	Loschmidt's <i>Umkehrwand</i> Revisited	241
			21.9	What is 'Equilibrium'?	242
			21.10	Entropy	242
			21.11	Interacting Particles	243

## Part IV Quantum Statistical Mechanics

<b>22 Quantum Ensembles</b>	247	<b>26 Ideal Quantum Gases</b>	308
22.1 Basic Quantum Mechanics	248	26.1 Single-Particle Quantum States	308
22.2 Energy Eigenstates	248	26.2 Density of Single-Particle States	310
22.3 Many-Body Systems	251	26.3 Many-Particle Quantum States	311
22.4 Two Types of Probability	252	26.4 Quantum Canonical Ensemble	312
22.5 The Density Matrix	254	26.5 Grand Canonical Ensemble	312
22.6 The Uniqueness of the Ensemble	255	26.6 A New Notation for Energy Levels	313
22.7 The Quantum Microcanonical Ensemble	256	26.7 Exchanging Sums and Products	315
<b>23 Quantum Canonical Ensemble</b>	258	26.8 Grand Canonical Partition Function for Independent Particles	315
23.1 Derivation of the QM Canonical Ensemble	258	26.9 Distinguishable Quantum Particles	316
23.2 Thermal Averages and the Average Energy	260	26.10 Sneaky Derivation of $PV = Nk_B T$	317
23.3 The Quantum Mechanical Partition Function	260	26.11 Equations for $U = \langle E \rangle$ and $\langle N \rangle$	318
23.4 The Quantum Mechanical Entropy	262	26.12 $\langle n_\epsilon \rangle$ for bosons	319
23.5 The Origin of the Third Law of Thermodynamics	264	26.13 $\langle n_\epsilon \rangle$ for fermions	319
23.6 Derivatives of Thermal Averages	266	26.14 Summary of Equations for Fermions and Bosons	320
23.7 Factorization of the Partition Function	266	26.15 Integral Form of Equations for $N$ and $U$	321
23.8 Special Systems	269	26.16 Basic Strategy for Fermions and Bosons	322
23.9 Two-Level Systems	269	26.17 $P = 2U/3V$	322
23.10 Simple Harmonic Oscillator	271	26.18 Problems	324
23.11 Einstein Model of a Crystal	273	<b>27 Bose–Einstein Statistics</b>	326
23.12 Problems	275	27.1 Basic Equations for Bosons	326
<b>24 Black-Body Radiation</b>	282	27.2 $\langle n_\epsilon \rangle$ for Bosons	326
24.1 Black Bodies	282	27.3 The Ideal Bose Gas	327
24.2 Universal Frequency Spectrum	282	27.4 Low-Temperature Behavior of $\mu$	328
24.3 A Simple Model	283	27.5 Bose–Einstein Condensation	329
24.4 Two Types of Quantization	283	27.6 Below the Einstein Temperature	330
24.5 Black-Body Energy Spectrum	285	27.7 Energy of an Ideal Gas of Bosons	331
24.6 Total Energy	288	27.8 What About the Second-Lowest Energy State?	332
24.7 Total Black-Body Radiation	289	27.9 The Pressure below $T < T_E$	333
24.8 Significance of Black-Body Radiation	289	27.10 Transition Line in $P$ - $V$ Plot	334
24.9 Problems	289	27.11 Problems	334
<b>25 The Harmonic Solid</b>	291	<b>28 Fermi–Dirac Statistics</b>	336
25.1 Model of an Harmonic Solid	291	28.1 Basic Equations for Fermions	336
25.2 Normal Modes	292	28.2 The Fermi Function and the Fermi Energy	337
25.3 Transformation of the Energy	296	28.3 A Useful Identity	338
25.4 The Frequency Spectrum	298	28.4 Systems with a Discrete Energy Spectrum	339
25.5 The Energy in the Classical Model	299	28.5 Systems with Continuous Energy Spectra	340
25.6 The Quantum Harmonic Crystal	300	28.6 Ideal Fermi Gas	340
25.7 Debye Approximation	301	28.7 Fermi Energy	340
25.8 Problems	306	28.8 Compressibility of Metals	341
		28.9 Sommerfeld Expansion	342
		28.10 General Fermi Gas at Low Temperatures	345

28.11	Ideal Fermi Gas at Low Temperatures	346
28.12	Problems	348
<b>29</b>	<b>Insulators and Semiconductors</b>	<b>351</b>
29.1	Tight-Binding Approximation	351
29.2	Bloch's Theorem	353
29.3	Nearly-Free Electrons	354
29.4	Energy Bands and Energy Gaps	357
29.5	Where is the Fermi Energy?	358
29.6	Fermi Energy in a Band (Metals)	358
29.7	Fermi Energy in a Gap	359
29.8	Intrinsic Semiconductors	362
29.9	Extrinsic Semiconductors	362
29.10	Semiconductor Statistics	364
29.11	Semiconductor Physics	367
<b>30</b>	<b>Phase Transitions and the Ising Model</b>	<b>368</b>
30.1	The Ising Chain	369
30.2	The Ising Chain in a Magnetic Field ( $J = 0$ )	369
30.3	The Ising Chain with $h = 0$ , but $J \neq 0$	371
30.4	The Ising Chain with both $J \neq 0$ and $h \neq 0$	372
30.5	Mean Field Approximation	376
30.6	Critical Exponents	380
30.7	Mean-Field Exponents	381
30.8	Analogy with the van der Waals Approximation	382
30.9	Landau Theory	383
30.10	Beyond Landau Theory	384
30.11	Problems	385
<b>Appendix:</b>	<b>Computer Calculations and VPython</b>	<b>390</b>
A.1	Histograms	390
A.2	The First VPython Program	391
A.3	VPython Functions	393
A.4	Graphs	393
A.5	Reporting VPython Results	395
A.6	Timing Your Program	397
A.7	Molecular Dynamics	397
A.8	Courage	398
<b>Index</b>		<b>399</b>