

# Contents

<b>Preface</b>	<b>viii</b>
<b>1 From Microscopic to Macroscopic Behavior</b>	<b>1</b>
1.1 Introduction . . . . .	1
1.2 Some Qualitative Observations . . . . .	2
1.3 Doing Work and the Quality of Energy . . . . .	4
1.4 Some Simple Simulations . . . . .	5
1.5 Measuring the Pressure and Temperature . . . . .	15
1.6 Work, Heating, and the First Law of Thermodynamics . . . . .	19
1.7 *The Fundamental Need for a Statistical Approach . . . . .	19
1.8 *Time and Ensemble Averages . . . . .	21
1.9 Models of Matter . . . . .	22
1.9.1 The ideal gas . . . . .	22
1.9.2 Interparticle potentials . . . . .	22
1.9.3 Lattice models . . . . .	23
1.10 Importance of Simulations . . . . .	23
1.11 Dimensionless Quantities . . . . .	24
1.12 Summary . . . . .	25
1.13 Supplementary Notes . . . . .	26
1.13.1 Approach to equilibrium . . . . .	26
1.13.2 Mathematics refresher . . . . .	27
Vocabulary . . . . .	27
Additional Problems . . . . .	28
Suggestions for Further Reading . . . . .	29

<b>2 Thermodynamic Concepts</b>	<b>31</b>
2.1 Introduction . . . . .	31
2.2 The System . . . . .	32
2.3 Thermodynamic Equilibrium . . . . .	32
2.4 Temperature . . . . .	34
2.5 Pressure Equation of State . . . . .	36
2.6 Some Thermodynamic Processes . . . . .	38
2.7 Work . . . . .	39
2.8 The First Law of Thermodynamics . . . . .	43
2.9 Energy Equation of State . . . . .	45
2.10 Heat Capacities and Enthalpy . . . . .	46
2.11 Quasistatic Adiabatic Processes . . . . .	49
2.12 The Second Law of Thermodynamics . . . . .	53
2.13 The Thermodynamic Temperature . . . . .	55
2.14 The Second Law and Heat Engines . . . . .	57
2.15 Entropy Changes . . . . .	64
2.16 Equivalence of Thermodynamic and Ideal Gas Scale Temperatures . . . . .	70
2.17 The Thermodynamic Pressure . . . . .	71
2.18 The Fundamental Thermodynamic Relation . . . . .	72
2.19 The Entropy of an Ideal Classical Gas . . . . .	74
2.20 The Third Law of Thermodynamics . . . . .	74
2.21 Free Energies . . . . .	75
2.22 Thermodynamic Derivatives . . . . .	80
2.23 *Applications to Irreversible Processes . . . . .	84
2.23.1 Joule or free expansion process . . . . .	85
2.23.2 Joule-Thomson process . . . . .	86
2.24 Supplementary Notes . . . . .	88
2.24.1 The mathematics of thermodynamics . . . . .	88
2.24.2 Thermodynamic potentials and Legendre transforms . . . . .	91
Vocabulary . . . . .	93
Additional Problems . . . . .	94
Suggestions for Further Reading . . . . .	103

<b>3</b>	<b>Concepts of Probability</b>	<b>106</b>
3.1	Probability in Everyday Life . . . . .	106
3.2	The Rules of Probability . . . . .	109
3.3	Mean Values . . . . .	113
3.4	The Meaning of Probability . . . . .	116
3.4.1	Information and uncertainty . . . . .	118
3.4.2	*Bayesian inference . . . . .	122
3.5	Bernoulli Processes and the Binomial Distribution . . . . .	127
3.6	Continuous Probability Distributions . . . . .	140
3.7	The Central Limit Theorem (or Why Thermodynamics Is Possible) . . . . .	144
3.8	*The Poisson Distribution or Should You Fly? . . . . .	147
3.9	*Traffic Flow and the Exponential Distribution . . . . .	148
3.10	*Are All Probability Distributions Gaussian? . . . . .	151
3.11	*Supplementary Notes . . . . .	153
3.11.1	Method of undetermined multipliers . . . . .	153
3.11.2	Derivation of the central limit theorem . . . . .	155
	Vocabulary . . . . .	159
	Additional Problems . . . . .	159
	Suggestions for Further Reading . . . . .	169
<b>4</b>	<b>Statistical Mechanics</b>	<b>172</b>
4.1	Introduction . . . . .	172
4.2	A Simple Example of a Thermal Interaction . . . . .	174
4.3	Counting Microstates . . . . .	184
4.3.1	Noninteracting spins . . . . .	184
4.3.2	A particle in a one-dimensional box . . . . .	185
4.3.3	One-dimensional harmonic oscillator . . . . .	188
4.3.4	One particle in a two-dimensional box . . . . .	188
4.3.5	One particle in a three-dimensional box . . . . .	190
4.3.6	Two noninteracting identical particles and the semiclassical limit . . . . .	191
4.4	The Number of States of Many Noninteracting Particles: Semiclassical Limit . . . . .	193
4.5	The Microcanonical Ensemble (Fixed $\mathbf{E}$ , $\mathbf{V}$ , and $\mathbf{N}$ ) . . . . .	194
4.6	The Canonical Ensemble (Fixed $\mathbf{T}$ , $\mathbf{V}$ , and $\mathbf{N}$ ) . . . . .	200
4.7	Connection Between Thermodynamics and Statistical Mechanics in the Canonical Ensemble	207
4.8	Simple Applications of the Canonical Ensemble . . . . .	208
4.9	An Ideal Thermometer . . . . .	211
4.10	Simulation of the Microcanonical Ensemble . . . . .	215

4.11	Simulation of the Canonical Ensemble . . . . .	216
4.12	Grand Canonical Ensemble (Fixed $T$ , $V$ , and $\mu$ ) . . . . .	217
4.13	*Entropy is not a Measure of Disorder . . . . .	219
4.14	Supplementary Notes . . . . .	221
4.14.1	The volume of a hypersphere . . . . .	221
4.14.2	Fluctuations in the canonical ensemble . . . . .	222
	Vocabulary . . . . .	223
	Additional Problems . . . . .	223
	Suggestions for Further Reading . . . . .	229
<b>5</b>	<b>Magnetic Systems</b> . . . . .	<b>230</b>
5.1	Paramagnetism . . . . .	230
5.2	Noninteracting Magnetic Moments . . . . .	231
5.3	Thermodynamics of Magnetism . . . . .	235
5.4	The Ising Model . . . . .	236
5.5	The Ising Chain . . . . .	237
5.5.1	Exact enumeration . . . . .	238
5.5.2	Spin-spin correlation function . . . . .	241
5.5.3	Simulations of the Ising chain . . . . .	244
5.5.4	*Transfer matrix . . . . .	245
5.5.5	Absence of a phase transition in one dimension . . . . .	248
5.6	The Two-Dimensional Ising Model . . . . .	248
5.6.1	Onsager solution . . . . .	249
5.6.2	Computer simulation of the two-dimensional Ising model . . . . .	254
5.7	Mean-Field Theory . . . . .	257
5.7.1	*Phase diagram of the Ising model . . . . .	263
5.8	*Simulation of the Density of States . . . . .	265
5.9	*Lattice Gas . . . . .	269
5.10	Supplementary Notes . . . . .	272
5.10.1	The Heisenberg model of magnetism . . . . .	272
5.10.2	Low temperature expansion . . . . .	274
5.10.3	High temperature expansion . . . . .	276
5.10.4	*Bethe approximation . . . . .	278
5.10.5	Fully connected Ising model . . . . .	281
5.10.6	Metastability and nucleation . . . . .	283
	Vocabulary . . . . .	285
	Additional Problems . . . . .	286

Suggestions for Further Reading . . . . .	291
<b>6 Many-Particle Systems</b>	<b>293</b>
6.1 The Ideal Gas in the Semiclassical Limit . . . . .	293
6.2 Classical Statistical Mechanics . . . . .	302
6.2.1 The equipartition theorem . . . . .	302
6.2.2 The Maxwell velocity distribution . . . . .	305
6.2.3 The Maxwell speed distribution . . . . .	307
6.3 Occupation Numbers and Bose and Fermi Statistics . . . . .	308
6.4 Distribution Functions of Ideal Bose and Fermi Gases . . . . .	310
6.5 Single Particle Density of States . . . . .	313
6.5.1 Photons . . . . .	314
6.5.2 Nonrelativistic particles . . . . .	315
6.6 The Equation of State of an Ideal Classical Gas: Application of the Grand Canonical Ensemble	317
6.7 Blackbody Radiation . . . . .	319
6.8 The Ideal Fermi Gas . . . . .	323
6.8.1 Ground state properties . . . . .	323
6.8.2 Low temperature properties . . . . .	327
6.9 The Heat Capacity of a Crystalline Solid . . . . .	332
6.9.1 The Einstein model . . . . .	332
6.9.2 Debye theory . . . . .	333
6.10 The Ideal Bose Gas and Bose Condensation . . . . .	335
6.11 Supplementary Notes . . . . .	340
6.11.1 Fluctuations in the number of particles . . . . .	340
6.11.2 Low temperature expansion of an ideal Fermi gas . . . . .	343
Vocabulary . . . . .	345
Additional Problems . . . . .	345
Suggestions for Further Reading . . . . .	354
<b>7 The Chemical Potential and Phase Equilibria</b>	<b>356</b>
7.1 Meaning of the chemical potential . . . . .	356
7.2 Measuring the chemical potential in simulations . . . . .	360
7.2.1 The Widom insertion method . . . . .	360
7.2.2 The chemical demon algorithm . . . . .	362
7.3 Phase Equilibria . . . . .	365
7.3.1 Equilibrium conditions . . . . .	366
7.3.2 Simple phase diagrams . . . . .	367

7.3.3	Clausius-Clapeyron equation . . . . .	369
7.4	The van der Waals Equation of State . . . . .	372
7.4.1	Maxwell construction . . . . .	372
7.4.2	*The van der Waals critical point . . . . .	379
7.5	*Chemical Reactions . . . . .	381
	Vocabulary . . . . .	385
	Additional Problems . . . . .	385
	Suggestions for Further Reading . . . . .	386
<b>8</b>	<b>Classical Gases and Liquids</b>	<b>388</b>
8.1	Introduction . . . . .	388
8.2	Density Expansion . . . . .	388
8.3	The Second Virial Coefficient . . . . .	392
8.4	*Diagrammatic Expansions . . . . .	397
8.4.1	Cumulants . . . . .	397
8.4.2	High temperature expansion . . . . .	398
8.4.3	Density expansion . . . . .	403
8.4.4	Higher order virial coefficients for hard spheres . . . . .	405
8.5	The Radial Distribution Function . . . . .	407
8.6	Perturbation Theory of Liquids . . . . .	413
8.6.1	The van der Waals equation . . . . .	416
8.7	*The Ornstein-Zernike Equation and Integral Equations for $g(\mathbf{r})$ . . . . .	417
8.8	*One-Component Plasma . . . . .	421
8.9	Supplementary Notes . . . . .	424
8.9.1	The third virial coefficient for hard spheres . . . . .	424
8.9.2	Definition of $g(\mathbf{r})$ in terms of the local particle density . . . . .	426
8.9.3	X-ray scattering and the static structure function . . . . .	427
	Vocabulary . . . . .	431
	Additional Problems . . . . .	431
	Suggestions for Further Reading . . . . .	434
<b>9</b>	<b>Critical Phenomena</b>	<b>435</b>
9.1	Landau Theory of Phase Transitions . . . . .	435
9.2	Universality and Scaling Relations . . . . .	442
9.3	A Geometrical Phase Transition . . . . .	444
9.4	Renormalization Group Method for Percolation . . . . .	450
9.5	The Renormalization Group Method and the One-Dimensional Ising Model . . . . .	454

9.6 *The Renormalization Group Method and the Two-Dimensional Ising Model . . .	458
Vocabulary . . . . .	464
Additional Problems . . . . .	464
Suggestions for Further Reading . . . . .	466
A.1 Physical Constants and Conversion Factors . . . . .	468
A.2 Hyperbolic Functions . . . . .	469
A.3 Approximations . . . . .	469
A.4 Euler-Maclaurin Formula . . . . .	469
A.5 Gaussian Integrals . . . . .	470
A.6 Stirling's Approximation . . . . .	471
A.7 Bernoulli Numbers . . . . .	472
A.8 Probability Distributions . . . . .	472
A.9 Fourier Transforms . . . . .	473
A.10 The Delta Function . . . . .	473
A.11 Convolution Integrals . . . . .	474
A.12 Fermi and Bose Integrals . . . . .	475