

CONTENTS

Preface	vii
Introduction	xxi
PART I EQUILIBRIUM	1
1 Equilibrium	2
1.1 Equilibrium and Observation Time	2
1.2 Equilibrium and Molecular Motion	4
1.3 Large Scale Change and Local Equilibrium	4
1.4 Structure of Matter	6
1.5 Supplement and Conclusions	8
Problems	9
2 The Basic Concepts of Thermodynamics	10
2.1 Equilibrium and Reversible Processes	10
2.2 Work and Heat	11
2.3 Adiabatic Process and Entropy	13
2.4 Absolute Temperature and Entropy	16
2.5 The Ideal Gas	19
2.6 The Second Law of Thermodynamics	24
2.7 The Efficiency and Speed of a Heat Engine	24
Problems	28

3	The Law of Detailed Balance	30
3.1	The Energy Distribution of the State	31
3.2	The Energy Distribution of Fermions	35
3.3	Conservation Laws, Chemical Potential and the Constant Term in the Entropy	39
3.4	Distribution of Bosons and Black Body Radiation	41
3.5	Chemical Reactions and the Law of Concentrations Problems	43 45
4	Electrons in Metals	48
4.1	Dense Ideal Gas	48
4.2	Heat Capacity	51
4.3	Influence of Periodic Structure	55
4.4	The Structural Change Caused by Electrons Problems	60 63
PART II	HYPOTHESIS	65
5	The Basic Assumption of Entropy and Molecular Motion	66
5.1	Region of Motion	66
5.2	Assumption for the Calculation of the Entropy	67
5.3	Fermions	70
5.4	The Ideal Gas	72
5.5	Some Special Features of High Dimensional Space	76
5.6	Peak Integration and the Law of Large Numbers	78
5.7	The Law of Equipartition of Energy	80
5.8	Perspectives of the Region of Motion	81
5.9	Trajectory and the Region of Motion Problems	85 86
6	Some Elementary Applications of the Basic Assumption	88
6.1	Systems and Subsystems	88
6.2	Vibrations	94
6.3	The Debye Model	98
6.4	Phonons and Second Sound	102

6.5	General Conclusions, Average Values and the Normal Distribution	111
	Problems	116
7	Rules of Calculation	118
7.1	Various Thermodynamic Potentials	118
7.2	The Various Rules of Calculation	122
	Problems	130
8	Illustrative Examples	133
8.1	Time Scale and the Region of Motion	133
8.2	Gas of Hydrogen Molecules	139
8.3	One-Dimensional Model	145
	Problems	150
9	Yang-Lee Theorem	153
9.1	Macroscopic Limit (i.e. Thermodynamic Limit)	154
9.2	Generalisation of the Theorem	159
	Problems	161
PART III	PROBABILITY	163
10	Probability and Statistics	164
10.1	The Use and Misuse of Probability	164
10.2	Distributions and the Statistics of the Average Value	166
10.3	The General Definition of Probability	174
	Problems	178
11	Independence and Chaos	180
11.1	The Definition and Consequence of Independent Phenomena	180
11.2	Test of Independence	186
11.3	Random Sequences	188
11.4	Scattering Experiments and the Measurement of the Correlation Functions	190
	Problems	195

12	Sum of Many Independent Variables	198
12.1	Normal Distributions	198
12.2	The Central Limit Theorem (Rudimentary Discussion)	200
12.3	Higher Order Averages and the Cumulant	203
12.4	The Cumulant Expansion Theorem	207
12.5	Central Limit Theorem (General Exposition)	209
12.6	Repeated Trials and the Determination of Probability	211
12.7	Random Motion and Diffusion	214
12.8	Fluctuation of Macroscopic Variables	217
12.9	Fluctuations and an Extension of the Basic Assumption	219
	Problems	222
13	Correlation Functions	225
13.1	Response and Fluctuation	225
13.2	Density Correlation Function	230
13.3	The Fermion Gas	235
13.4	The Response and Correlation Functions in Quantum Mechanics	238
	Problems	242
PART IV	APPLICATIONS	245
14	Corrections to the Ideal Gas Law	246
14.1	Intermolecular Interactions	246
14.2	Corrections to the Ideal Gas Law	248
14.3	Time Delay in Collisions	250
14.4	Quantum Mechanical Calculation	254
14.5	Bound State and the Levinson Theorem	257
	Problems	259
15	Phase Equilibrium	261
15.1	Gaseous and Liquid Phases	261
15.2	The Growth of Water Droplets	265
15.3	Latent Heat and the Interaction Energy of Molecules	268
15.4	Melting and the Lindemann Formula	270
15.5	Definitions of μ_1 and μ_2	271
	Problems	274

16	Magnetism	277
16.1	Paramagnetism	277
16.2	Magnetic Susceptibility	281
16.3	Diamagnetism of Charged Particles	283
16.4	Spin-spin Interaction	291
	Problems	295
17	Ising Model	297
17.1	Ising Ferromagnetism in One Dimension	297
17.2	Proof of the Existence of Ising Ferromagnetism in Two Dimensions	301
17.3	Other Ising Models	307
	Problems	310
18	Impurities and Motion	312
18.1	Solutions and Osmotic Pressure	312
18.2	Effective Interaction Energy	314
18.3	Low Density Case	316
18.4	Mobile and Stationary Impurities	318
18.5	The Amorphous State	323
	Problems	325
19	Electrostatic Interaction	329
19.1	Short Distance and Long Distance are Both Important	329
19.2	The Plasma Gas and Ionic Solutions	330
19.3	Electrons in Metals	333
19.4	Electron Crystals	335
19.5	Two-Dimensional Coulomb Gas Model	337
	Problems	341
PART V	DYNAMICS	345
20	The Equation of Motion For Gases	346
20.1	Flow and Collision	346
20.2	Case of No Collisions — Plasma Oscillations	349
20.3	Zero Sound	351
20.4	Collisions and Diffusion	354

xviii STATISTICAL MECHANICS

20.5	Collisions and Sound Waves, Viscosity and Heat Conduction	357
20.6	<i>H</i> -theorem	363
	Problems	364
21	The Diffusion Equation	367
21.1	Simple Examples	367
21.2	The Metastable State	372
21.3	Transformation to the Wave Equation	374
21.4	Derivation of the Diffusion Equation	376
21.5	Two-State Cluster Model	380
	Problems	386
22	Numerical Simulation	388
22.1	Numerical Solution of Molecular Motion	389
22.2	Random Sequences	391
22.3	Monte Carlo Simulation	391
22.4	Conceptual Problems to be Noted	394
	Problems	397
PART VI	THEORETICAL BASES	399
23	Laws of Thermodynamics	400
23.1	Adiabatic Processes	400
23.2	Adiabatic Process and Entropy	403
23.3	The Second Law of Thermodynamics	405
23.4	The Third Law of Thermodynamics	408
23.5	The Amorphous State and the Third Law	411
	Problems	413
24	Echo Phenomena	415
24.1	Demonstration of the Viscous Liquid Bottle	416
24.2	Analysis of the Demonstration	417
24.3	Spin Echo Experiment	419
24.4	The Plasma Echo	422
	Problems	424

25	Entropy Calculation from the Trajectory of Motion	425
25.1	Number of Coincidences and the Size of the Region	426
25.2	Independence of Different Parts of a System	429
25.3	Correlation Time	431
25.4	Process of Computation	432
25.5	Entropy of the Metastable State	434
25.6	The Third Law of Thermodynamics	435
	Problems	437
26	The Origin of the Basic Assumption	440
26.1	The Basic Assumption	441
26.2	Ergodicity and Ensembles	442
26.3	Mixing and Independence	445
26.4	Probability and Experiments	448
26.5	Instability of the Trajectory	450
26.6	The General Problem of Independence	454
26.7	Difficulties Encountered in Applications	455
	Problems	455
PART VII	CONDENSATION	457
27	Mean Field Solutions	458
27.1	Mean Field Theory	458
27.2	Total Magnetic Moment	461
27.3	Thermodynamical Potential and the Coexistence of Different Phases	464
27.4	The Ising Lattice Gas	466
27.5	The Van der Waals Equation	470
27.6	Common Properties of Condensation Phenomena	473
	Problems	476
28	Fluctuation of the Boundary Surface	480
28.1	The Liquid Surface Model	481
28.2	The Boundary Surface of the Ising Model	485
28.3	Crystal Surface — the Coulomb Gas Model	488
	Problems	493

29	Models with Continuous Symmetry	495
29.1	The Planar Vector Model	495
29.2	Density Fluctuations of a Crystal	498
29.3	Quantum Vector Model	502
29.4	Continuous Symmetry and Soft Modes	505
29.5	Defects in the Condensation	508
	Problems	514
30	Theory of Superfluidity	518
30.1	Quantum Lattice Gas	519
30.2	The Ground State and Low Temperature Model	522
30.3	State of Flow and Winding Number	525
30.4	Stability of Superfluidity	528
	Problems	535
	References	541
	Index	545