
Contents

Part I General Principles

1	Thermal Equilibrium and the Principle of Equal Probability	3
1.1	Introduction to Thermal and Statistical Physics	3
1.2	Thermal Equilibrium	4
1.2.1	Description of a System in Equilibrium	4
1.2.2	State Variables, Work, and Heat	5
1.2.3	Temperature and the Zeroth Law of Thermodynamics ..	7
1.2.4	Heat Capacity and Specific Heat	8
1.3	Kinetic Theory of Gas Molecules	9
1.3.1	The Spatial Distribution of Gas Molecules	10
1.3.2	Velocity Distribution of an Ideal Gas	15
1.3.3	The Pressure of a Gas	18
1.4	The Principle of Equal Probability	20
2	Entropy	23
2.1	The Microcanonical Distribution	23
2.2	Number of States and Density of States	26
2.3	Conditions for Thermal Equilibrium	28
2.3.1	Equilibrium Condition when only Energy is Exchanged	28
2.3.2	Equilibrium Condition when Molecules are Exchanged .	30
2.3.3	Equilibrium Condition when Two Systems Share a Common Volume	31
2.4	Thermal Nonequilibrium and Irreversible Processes	32
3	The Partition Function and the Free Energy	35
3.1	A System in a Heat Bath	35
3.1.1	Canonical Distribution	36
3.1.2	Application to a Molecule in Gas	37

3.2	Partition Function	38
3.3	Free Energy	39
3.4	Internal Energy	41
3.5	Thermodynamic Functions and Legendre Transformations	42
3.6	Maxwell Relations	43

Part II Elementary Applications

4	Ideal Gases	47
4.1	Quantum Mechanics of a Gas Molecule	47
4.2	Phase Space and the Number of Microscopic States	49
4.3	Entropy of an Ideal Gas	51
4.4	Pressure of an Ideal Gas: Quantum Mechanical Treatment	54
4.5	Statistical-Mechanical Temperature and Pressure	55
4.6	Partition Function of an Ideal Gas	56
4.7	Diatomic Molecules	58
4.7.1	Decomposition of the Partition Function	58
4.7.2	Center-of-Gravity Part: $Z^{(\text{CG})}$	60
4.7.3	Vibrational Part: $Z^{(\text{V})}$	61
4.7.4	Rotational Part: $Z^{(\text{R})}$	64
5	The Heat Capacity of a Solid, and Black-Body Radiation	67
5.1	Heat Capacity of a Solid I – Einstein Model	67
5.2	Heat Capacity of a Solid II – Debye Model	70
5.2.1	Collective Oscillations of the Lattice and the Internal Energy	70
5.2.2	Heat Capacity at High Temperature	73
5.2.3	Heat Capacity at Low Temperature	74
5.2.4	Heat Capacity at Intermediate Temperature	74
5.2.5	Physical Explanation for the Temperature Dependence	75
5.3	Black-Body Radiation	76
5.3.1	Wien’s Law and Stefan’s Law	76
5.3.2	Energy of Radiation in a Cavity	77
5.3.3	Spectrum of Light Emitted from a Hole	78
5.3.4	The Temperature of the Universe	80
6	The Elasticity of Rubber	83
6.1	Characteristics of Rubber	83
6.2	Model of Rubber	84
6.3	Entropy of Rubber	85
6.4	Hooke’s Law	86

7	Magnetic Materials	89
7.1	Origin of Permanent Magnetism	89
7.2	Statistical Mechanics of a Free Spin System	91
7.2.1	Model and Entropy	91
7.2.2	Free Energy, Magnetization, and Susceptibility	93
7.2.3	Internal Energy and Heat Capacity	95
7.3	Ising Model – Mean-Field Approximation	97
7.3.1	Links	97
7.3.2	Mean-Field Approximation	99
7.3.3	Solution of the Self-Consistent Equation	100
7.3.4	Entropy and Heat Capacity	103
7.3.5	Susceptibility	105
7.3.6	Domain Structure	106
7.4	The One-Dimensional Ising Model	106
7.4.1	Free Energy	106
7.4.2	Entropy and Heat Capacity	108
7.4.3	Magnetization and Susceptibility	110

Part III More Advanced Topics

8	First-Order Phase Transitions	115
8.1	The Various Phases of Matter	115
8.2	System in a Heat Bath at Fixed P and T	119
8.3	Coexistence of Phases	121
8.4	The Clausius–Clapeyron Law	123
8.5	The Critical Point	126
8.6	The van der Waals Gas	128
8.6.1	Coexistence of Gas and Liquid	130
9	Second-Order Phase Transitions	133
9.1	Various Phase Transitions and Order Parameters	133
9.2	Landau Theory	134
9.2.1	Free Energy	137
9.2.2	Entropy, Internal Energy, and Heat Capacity	138
9.2.3	Critical Phenomena	139
9.3	The Two-Dimensional Ising Model	140
10	Dense Gases – Ideal Gases at Low Temperature	147
10.1	The Phase Space for N Identical Particles	147
10.2	The Grand Canonical Distribution	149
10.3	Ideal Fermi Gases and Ideal Bose Gases	151
10.3.1	Occupation Number Representation	151
10.3.2	Thermodynamic Functions	154

10.4 Properties of a Free-Fermion Gas 154
 10.4.1 Properties at $T = 0$ 157
 10.4.2 Properties at Low Temperature 160
10.5 Properties of a Free-Boson Gas 169
 10.5.1 The Two Kinds of Bose Gas 169
 10.5.2 Properties at Low Temperature 170
10.6 Properties of Gases at High Temperature 178

Part IV Appendices

A Formulas Related to the Factorial Function 185
 A.1 Binomial Coefficients and Binomial Theorem 185
 A.2 Stirling's Formula 185
 A.3 $n!$ 186

B The Gaussian Distribution Function 187
 B.1 The Central Limit Theorem 187
 B.1.1 Example 188
 B.2 Gaussian Integrals 188
 B.3 The Fourier Transform of a Gaussian Distribution Function ... 189

C Lagrange's Method of Undetermined Multipliers 191
 C.1 Example 192
 C.2 Generalization 192

D Volume of a Hypersphere 193

E Hyperbolic Functions 195

F Boundary Conditions 197
 F.1 Fixed Boundary Condition 197
 F.2 Periodic Boundary Condition 198

G The Riemann Zeta Function 201

References 203

Index 205