

Table of Contents

1. Basic Principles	1
1.1 Introduction	1
1.2 A Brief Excursion into Probability Theory	4
1.2.1 Probability Density and Characteristic Functions	4
1.2.2 The Central Limit Theorem	7
1.3 Ensembles in Classical Statistics	9
1.3.1 Phase Space and Distribution Functions	9
1.3.2 The Liouville Equation	11
1.4 Quantum Statistics	14
1.4.1 The Density Matrix for Pure and Mixed Ensembles ...	14
1.4.2 The Von Neumann Equation	15
*1.5 Additional Remarks	16
*1.5.1 The Binomial and the Poisson Distributions	16
*1.5.2 Mixed Ensembles and the Density Matrix of Subsystems	19
Problems	21
 2. Equilibrium Ensembles	 25
2.1 Introductory Remarks	25
2.2 Microcanonical Ensembles	26
2.2.1 Microcanonical Distribution Functions and Density Matrices	26
2.2.2 The Classical Ideal Gas	30
*2.2.3 Quantum-mechanical Harmonic Oscillators and Spin Systems	33
2.3 Entropy	35
2.3.1 General Definition	35
2.3.2 An Extremal Property of the Entropy	36
2.3.3 Entropy of the Microcanonical Ensemble	37
2.4 Temperature and Pressure	38
2.4.1 Systems in Contact: the Energy Distribution Function, Definition of the Temperature	38

2.4.2	On the Widths of the Distribution Functions of Macroscopic Quantities	41
2.4.3	External Parameters: Pressure	42
2.5	Properties of Some Non-interacting Systems	46
2.5.1	The Ideal Gas	46
*2.5.2	Non-interacting Quantum Mechanical Harmonic Oscillators and Spins	48
2.6	The Canonical Ensemble	50
2.6.1	The Density Matrix	50
2.6.2	Examples: the Maxwell Distribution and the Barometric Pressure Formula	53
2.6.3	The Entropy of the Canonical Ensemble and Its Extremal Values	54
2.6.4	The Virial Theorem and the Equipartition Theorem . .	54
2.6.5	Thermodynamic Quantities in the Canonical Ensemble	58
2.6.6	Additional Properties of the Entropy	60
2.7	The Grand Canonical Ensemble	63
2.7.1	Systems with Particle Exchange	63
2.7.2	The Grand Canonical Density Matrix	64
2.7.3	Thermodynamic Quantities	65
2.7.4	The Grand Partition Function for the Classical Ideal Gas	67
*2.7.5	The Grand Canonical Density Matrix in Second Quantization	69
	Problems	70
3.	Thermodynamics	75
3.1	Potentials and Laws of Equilibrium Thermodynamics	75
3.1.1	Definitions	75
3.1.2	The Legendre Transformation	79
3.1.3	The Gibbs–Duhem Relation in Homogeneous Systems .	81
3.2	Derivatives of Thermodynamic Quantities	82
3.2.1	Definitions	82
3.2.2	Integrability and the Maxwell Relations	84
3.2.3	Jacobians	87
3.2.4	Examples	88
3.3	Fluctuations and Thermodynamic Inequalities	89
3.3.1	Fluctuations	89
3.3.2	Inequalities	90
3.4	Absolute Temperature and Empirical Temperatures	91
3.5	Thermodynamic Processes	92
3.5.1	Thermodynamic Concepts	93
3.5.2	The Irreversible Expansion of a Gas; the Gay-Lussac Experiment	95
3.5.3	The Statistical Foundation of Irreversibility	97

3.5.4	Reversible Processes	98
3.5.5	The Adiabatic Equation	102
3.6	The First and Second Laws of Thermodynamics	103
3.6.1	The First and the Second Law for Reversible and Irreversible Processes	103
*3.6.2	Historical Formulations of the Laws of Thermodynamics and other Remarks . .	107
3.6.3	Examples and Supplements to the Second Law	109
3.6.4	Extremal Properties	120
*3.6.5	Thermodynamic Inequalities Derived from Maximization of the Entropy	123
3.7	Cyclic Processes	125
3.7.1	General Considerations	125
3.7.2	The Carnot Cycle	126
3.7.3	General Cyclic Processes	128
3.8	Phases of Single-Component Systems	130
3.8.1	Phase-Boundary Curves	130
3.8.2	The Clausius–Clapeyron Equation	134
3.8.3	The Convexity of the Free Energy and the Concavity of the Free Enthalpy (Gibbs’ Free Energy)	139
3.8.4	The Triple Point	141
3.9	Equilibrium in Multicomponent Systems	144
3.9.1	Generalization of the Thermodynamic Potentials	144
3.9.2	Gibbs’ Phase Rule and Phase Equilibrium	146
3.9.3	Chemical Reactions, Thermodynamic Equilibrium and the Law of Mass Action	150
*3.9.4	Vapor-pressure Increase by Other Gases and by Surface Tension	156
	Problems	160
4.	Ideal Quantum Gases	169
4.1	The Grand Potential	169
4.2	The Classical Limit $z = e^{\mu/kT} \ll 1$	175
4.3	The Nearly-degenerate Ideal Fermi Gas	176
4.3.1	Ground State, $T = 0$ (Degeneracy)	177
4.3.2	The Limit of Complete Degeneracy	178
*4.3.3	Real Fermions	185
4.4	The Bose–Einstein Condensation	190
4.5	The Photon Gas	197
4.5.1	Properties of Photons	197
4.5.2	The Canonical Partition Function	199
4.5.3	Planck’s Radiation Law	200
*4.5.4	Supplemental Remarks	204
*4.5.5	Fluctuations in the Particle Number of Fermions and Bosons	205

4.6	Phonons in Solids	206
4.6.1	The Harmonic Hamiltonian	206
4.6.2	Thermodynamic Properties	209
*4.6.3	Anharmonic Effects, the Mie-Grüneisen Equation of State	211
4.7	Phonons und Rotons in He II	213
4.7.1	The Excitations (Quasiparticles) of He II	213
4.7.2	Thermal Properties	215
*4.7.3	Superfluidity and the Two-Fluid Model	217
	Problems	221
5.	Real Gases, Liquids, and Solutions	225
5.1	The Ideal Molecular Gas	225
5.1.1	The Hamiltonian and the Partition Function	225
5.1.2	The Rotational Contribution	227
5.1.3	The Vibrational Contribution	230
*5.1.4	The Influence of the Nuclear Spin	232
*5.2	Mixtures of Ideal Molecular Gases	234
5.3	The Virial Expansion	236
5.3.1	Derivation	236
5.3.2	The Classical Approximation for the Second Virial Coefficient	238
5.3.3	Quantum Corrections to the Virial Coefficients	241
5.4	The Van der Waals Equation of State	242
5.4.1	Derivation	242
5.4.2	The Maxwell Construction	247
5.4.3	The Law of Corresponding States	251
5.4.4	The Vicinity of the Critical Point	251
5.5	Dilute Solutions	257
5.5.1	The Partition Function and the Chemical Potentials ..	257
5.5.2	Osmotic Pressure	261
*5.5.3	Solutions of Hydrogen in Metals (Nb, Pd,...)	262
5.5.4	Freezing-Point Depression, Boiling-Point Elevation, and Vapor-Pressure Reduction	263
	Problems	266
6.	Magnetism	269
6.1	The Density Matrix and Thermodynamics	269
6.1.1	The Hamiltonian and the Canonical Density Matrix ..	269
6.1.2	Thermodynamic Relations	273
6.1.3	Supplementary Remarks	276
6.2	The Diamagnetism of Atoms	278
6.3	The Paramagnetism of Non-coupled Magnetic Moments	280
6.4	Pauli Spin Paramagnetism	284

6.5	Ferromagnetism	287
6.5.1	The Exchange Interaction	287
6.5.2	The Molecular Field Approximation for the Ising Model	289
6.5.3	Correlation Functions and Susceptibility	300
6.5.4	The Ornstein–Zernike Correlation Function	301
*6.5.5	Continuum Representation	305
*6.6	The Dipole Interaction, Shape Dependence, Internal and External Fields	307
6.6.1	The Hamiltonian	307
6.6.2	Thermodynamics and Magnetostatics	308
6.6.3	Statistical–Mechanical Justification	312
6.6.4	Domains	316
6.7	Applications to Related Phenomena	317
6.7.1	Polymers and Rubber-like Elasticity	317
6.7.2	Negative Temperatures	320
*6.7.3	The Melting Curve of ^3He	323
	Problems	325
7.	Phase Transitions, Renormalization Group Theory, and Percolation	331
7.1	Phase Transitions and Critical Phenomena	331
7.1.1	Symmetry Breaking, the Ehrenfest Classification	331
*7.1.2	Examples of Phase Transitions and Analogies	332
7.1.3	Universality	338
7.2	The Static Scaling Hypothesis	339
7.2.1	Thermodynamic Quantities and Critical Exponents	339
7.2.2	The Scaling Hypothesis for the Correlation Function	343
7.3	The Renormalization Group	345
7.3.1	Introductory Remarks	345
7.3.2	The One-Dimensional Ising Model, Decimation Transformation	346
7.3.3	The Two-Dimensional Ising Model	349
7.3.4	Scaling Laws	356
*7.3.5	General RG Transformations in Real Space	359
*7.4	The Ginzburg–Landau Theory	361
7.4.1	Ginzburg–Landau Functionals	361
7.4.2	The Ginzburg–Landau Approximation	364
7.4.3	Fluctuations in the Gaussian Approximation	366
7.4.4	Continuous Symmetry and Phase Transitions of First Order	373
*7.4.5	The Momentum-Shell Renormalization Group	380
*7.5	Percolation	387
7.5.1	The Phenomenon of Percolation	387
7.5.2	Theoretical Description of Percolation	391

7.5.3	Percolation in One Dimension	392
7.5.4	The Bethe Lattice (Cayley Tree)	393
7.5.5	General Scaling Theory	398
7.5.6	Real-Space Renormalization Group Theory	400
	Problems	404
8.	Brownian Motion, Equations of Motion and the Fokker–Planck Equations	409
8.1	Langevin Equations	409
8.1.1	The Free Langevin Equation	409
8.1.2	The Langevin Equation in a Force Field	414
8.2	The Derivation of the Fokker–Planck Equation from the Langevin Equation	416
8.2.1	The Fokker–Planck Equation for the Langevin Equation (8.1.1)	416
8.2.2	Derivation of the Smoluchowski Equation for the Overdamped Langevin Equation, (8.1.23)	418
8.2.3	The Fokker–Planck Equation for the Langevin Equation (8.1.22b)	420
8.3	Examples and Applications	420
8.3.1	Integration of the Fokker–Planck Equation (8.2.6)	420
8.3.2	Chemical Reactions	422
8.3.3	Critical Dynamics	425
*8.3.4	The Smoluchowski Equation and Supersymmetric Quantum Mechanics	429
	Problems	432
9.	The Boltzmann Equation	437
9.1	Introduction	437
9.2	Derivation of the Boltzmann Equation	438
9.3	Consequences of the Boltzmann Equation	443
9.3.1	The H -Theorem and Irreversibility	443
*9.3.2	Behavior of the Boltzmann Equation under Time Reversal	446
9.3.3	Collision Invariants and the Local Maxwell Distribution	447
9.3.4	Conservation Laws	449
9.3.5	The Hydrodynamic Equations in Local Equilibrium	451
*9.4	The Linearized Boltzmann Equation	455
9.4.1	Linearization	455
9.4.2	The Scalar Product	457
9.4.3	Eigenfunctions of \mathcal{L} and the Expansion of the Solutions of the Boltzmann Equation	458

9.4.4	The Hydrodynamic Limit	460
9.4.5	Solutions of the Hydrodynamic Equations	466
*9.5	Supplementary Remarks	468
9.5.1	Relaxation-Time Approximation	468
9.5.2	Calculation of $W(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}'_1, \mathbf{v}'_2)$	469
	Problems	476
10.	Irreversibility and the Approach to Equilibrium	479
10.1	Preliminary Remarks	479
10.2	Recurrence Time	481
10.3	The Origin of Irreversible Macroscopic Equations of Motion	484
10.3.1	A Microscopic Model for Brownian Motion	484
10.3.2	Microscopic Time-Reversible and Macroscopic Irreversible Equations of Motion, Hydrodynamics	490
*10.4	The Master Equation and Irreversibility in Quantum Mechanics	491
10.5	Probability and Phase-Space Volume	494
*10.5.1	Probabilities and the Time Interval of Large Fluctuations	494
10.5.2	The Ergodic Theorem	497
10.6	The Gibbs and the Boltzmann Entropies and their Time Dependences	498
10.6.1	The Time Derivative of Gibbs' Entropy	498
10.6.2	Boltzmann's Entropy	498
10.7	Irreversibility and Time Reversal	500
10.7.1	The Expansion of a Gas	500
10.7.2	Description of the Expansion Experiment in μ -Space ..	505
10.7.3	The Influence of External Perturbations on the Trajectories of the Particles	506
*10.8	Entropy Death or Ordered Structures?	507
	Problems	509
Appendix	513
A.	Nernst's Theorem (Third Law)	513
A.1	Preliminary Remarks on the Historical Development of Nernst's Theorem	513
A.2	Nernst's Theorem and its Thermodynamic Consequences	514
A.3	Residual Entropy, Metastability, etc.	516
B.	The Classical Limit and Quantum Corrections	521
B.1	The Classical Limit	521

XVIII Table of Contents

B.2	Calculation of the Quantum-Mechanical Corrections ..	526
B.3	Quantum Corrections to the Second Virial Coefficient $B(T)$	531
C.	The Perturbation Expansion	536
D.	The Riemann ζ -Function and the Bernoulli Numbers.....	537
E.	Derivation of the Ginzburg–Landau Functional.....	538
F.	The Transfer Matrix Method.....	545
G.	Integrals Containing the Maxwell Distribution	547
H.	Hydrodynamics	548
H.1	Hydrodynamic Equations, Phenomenological Discussion	549
H.2	The Kubo Relaxation Function.....	550
H.3	The Microscopic Derivation of the Hydrodynamic Equations	552
I.	Units and Tables	557
Subject Index		565

Statistical Mechanics

Schwabl, F.

2006, XVIII, 578 p. 202 illus., Hardcover

ISBN: 978-3-540-32343-3