

# Contents

<b>1</b>	<b>Classical mechanics</b>	1
1.1	Introduction	1
1.2	Newton's laws of motion	1
1.3	Phase space: visualizing classical motion	5
1.4	Lagrangian formulation of classical mechanics: A general framework for Newton's laws	9
1.5	Legendre transforms	16
1.6	Generalized momenta and the Hamiltonian formulation of classical mechanics	17
1.7	A simple classical polymer model	24
1.8	The action integral	28
1.9	Lagrangian mechanics and systems with constraints	31
1.10	Gauss's principle of least constraint	34
1.11	Rigid body motion: Euler angles and quaternions	36
1.12	Non-Hamiltonian systems	46
1.13	Problems	49
<b>2</b>	<b>Theoretical foundations of classical statistical mechanics</b>	53
2.1	Overview	53
2.2	The laws of thermodynamics	55
2.3	The ensemble concept	61
2.4	Phase space volumes and Liouville's theorem	63
2.5	The ensemble distribution function and the Liouville equation	65
2.6	Equilibrium solutions of the Liouville equation	69
2.7	Problems	70
<b>3</b>	<b>The microcanonical ensemble and introduction to molecular dynamics</b>	74
3.1	Brief overview	74
3.2	Basic thermodynamics, Boltzmann's relation, and the partition function of the microcanonical ensemble	75
3.3	The classical virial theorem	80
3.4	Conditions for thermal equilibrium	83
3.5	The free particle and the ideal gas	86
3.6	The harmonic oscillator and harmonic baths	92
3.7	Introduction to molecular dynamics	95
3.8	Integrating the equations of motion: Finite difference methods	98
3.9	Systems subject to holonomic constraints	103
3.10	The classical time evolution operator and numerical integrators	106
3.11	Multiple time-scale integration	113

3.12 Symplectic integration for quaternions	117
3.13 Exactly conserved time step dependent Hamiltonians	120
3.14 Illustrative examples of molecular dynamics calculations	123
3.15 Problems	129
<b>4 The canonical ensemble</b>	133
4.1 Introduction: A different set of experimental conditions	133
4.2 Thermodynamics of the canonical ensemble	134
4.3 The canonical phase space distribution and partition function	135
4.4 Energy fluctuations in the canonical ensemble	140
4.5 Simple examples in the canonical ensemble	142
4.6 Structure and thermodynamics in real gases and liquids from spatial distribution functions	151
4.7 Perturbation theory and the van der Waals equation	166
4.8 Molecular dynamics in the canonical ensemble: Hamiltonian formulation in an extended phase space	177
4.9 Classical non-Hamiltonian statistical mechanics	183
4.10 Nosé–Hoover chains	188
4.11 Integrating the Nosé–Hoover chain equations	194
4.12 The isokinetic ensemble: A simple variant of the canonical ensemble	199
4.13 Applying the canonical molecular dynamics: Liquid structure	204
4.14 Problems	205
<b>5 The isobaric ensembles</b>	214
5.1 Why constant pressure?	214
5.2 Thermodynamics of isobaric ensembles	215
5.3 Isobaric phase space distributions and partition functions	216
5.4 Pressure and work virial theorems	222
5.5 An ideal gas in the isothermal-isobaric ensemble	224
5.6 Extending of the isothermal-isobaric ensemble: Anisotropic cell fluctuations	225
5.7 Derivation of the pressure tensor estimator from the canonical partition function	228
5.8 Molecular dynamics in the isoenthalpic-isobaric ensemble	233
5.9 Molecular dynamics in the isothermal-isobaric ensemble I: Isotropic volume fluctuations	236
5.10 Molecular dynamics in the isothermal-isobaric ensemble II: Anisotropic cell fluctuations	239
5.11 Atomic and molecular virials	243
5.12 Integrating the MTK equations of motion	245
5.13 The isothermal-isobaric ensemble with constraints: The ROLL algorithm	252
5.14 Problems	257
<b>6 The grand canonical ensemble</b>	261
6.1 Introduction: The need for yet another ensemble	261

6.2	Euler's theorem	261
6.3	Thermodynamics of the grand canonical ensemble	263
6.4	Grand canonical phase space and the partition function	264
6.5	Illustration of the grand canonical ensemble: The ideal gas	270
6.6	Particle number fluctuations in the grand canonical ensemble	271
6.7	Problems	274
<b>7</b>	<b>Monte Carlo</b>	<b>277</b>
7.1	Introduction to the Monte Carlo method	277
7.2	The Central Limit theorem	278
7.3	Sampling distributions	282
7.4	Hybrid Monte Carlo	294
7.5	Replica exchange Monte Carlo	297
7.6	Wang–Landau sampling	301
7.7	Transition path sampling and the transition path ensemble	302
7.8	Problems	309
<b>8</b>	<b>Free energy calculations</b>	<b>312</b>
8.1	Free energy perturbation theory	312
8.2	Adiabatic switching and thermodynamic integration	315
8.3	Adiabatic free energy dynamics	319
8.4	Jarzynski's equality and nonequilibrium methods	322
8.5	The problem of rare events	330
8.6	Reaction coordinates	331
8.7	The blue moon ensemble approach	333
8.8	Umbrella sampling and weighted histogram methods	340
8.9	Wang–Landau sampling	344
8.10	Adiabatic dynamics	345
8.11	Metadynamics	352
8.12	The committor distribution and the histogram test	356
8.13	Problems	358
<b>9</b>	<b>Quantum mechanics</b>	<b>362</b>
9.1	Introduction: Waves and particles	362
9.2	Review of the fundamental postulates of quantum mechanics	364
9.3	Simple examples	377
9.4	Identical particles in quantum mechanics: Spin statistics	383
9.5	Problems	386
<b>10</b>	<b>Quantum ensembles and the density matrix</b>	<b>391</b>
10.1	The difficulty of many-body quantum mechanics	391
10.2	The ensemble density matrix	392
10.3	Time evolution of the density matrix	395
10.4	Quantum equilibrium ensembles	396
10.5	Problems	401
<b>11</b>	<b>The quantum ideal gases: Fermi–Dirac and Bose–Einstein statistics</b>	<b>405</b>

11.1 Complexity without interactions	405
11.2 General formulation of the quantum-mechanical ideal gas	405
11.3 An ideal gas of distinguishable quantum particles	409
11.4 General formulation for fermions and bosons	411
11.5 The ideal fermion gas	413
11.6 The ideal boson gas	428
11.7 Problems	438
<b>12 The Feynman path integral</b>	442
12.1 Quantum mechanics as a sum over paths	442
12.2 Derivation of path integrals for the canonical density matrix and the time evolution operator	446
12.3 Thermodynamics and expectation values from the path integral	453
12.4 The continuous limit: Functional integrals	458
12.5 Many-body path integrals	467
12.6 Numerical evaluation of path integrals	471
12.7 Problems	487
<b>13 Classical time-dependent statistical mechanics</b>	491
13.1 Ensembles of driven systems	491
13.2 Driven systems and linear response theory	493
13.3 Applying linear response theory: Green–Kubo relations for transport coefficients	500
13.4 Calculating time correlation functions from molecular dynamics	508
13.5 The nonequilibrium molecular dynamics approach	513
13.6 Problems	523
<b>14 Quantum time-dependent statistical mechanics</b>	526
14.1 Time-dependent systems in quantum mechanics	526
14.2 Time-dependent perturbation theory in quantum mechanics	530
14.3 Time correlation functions and frequency spectra	540
14.4 Examples of frequency spectra	545
14.5 Quantum linear response theory	548
14.6 Approximations to quantum time correlation functions	554
14.7 Problems	564
<b>15 The Langevin and generalized Langevin equations</b>	568
15.1 The general model of a system plus a bath	568
15.2 Derivation of the generalized Langevin equation	571
15.3 Analytically solvable examples based on the GLE	579
15.4 Vibrational dephasing and energy relaxation in simple fluids	584
15.5 Molecular dynamics with the Langevin equation	587
15.6 Sampling stochastic transition paths	592
15.7 Mori–Zwanzig theory	594
15.8 Problems	600
<b>16 Critical phenomena</b>	605
16.1 Phase transitions and critical points	605

16.2 The critical exponents $\alpha$ , $\beta$ , $\gamma$ , and $\delta$	607
16.3 Magnetic systems and the Ising model	608
16.4 Universality classes	613
16.5 Mean-field theory	614
16.6 Ising model in one dimension	620
16.7 Ising model in two dimensions	622
16.8 Spin correlations and their critical exponents	629
16.9 Introduction to the renormalization group	630
16.10 Fixed points of the RG equations in greater than one dimension	637
16.11 General linearized RG theory	639
16.12 Understanding universality from the linearized RG theory	641
16.13 Problems	643
<b>Appendix A Properties of the Dirac delta-function</b>	649
<b>Appendix B Evaluation of energies and forces</b>	652
<b>Appendix C Proof of the Trotter theorem</b>	663
<b>Appendix D Laplace transforms</b>	666
<b>References</b>	671
<b>Index</b>	687