

# Contents

Preface to the third edition	xv
Preface to the second edition	xix
Preface to first edition	xxi

## 1. Introduction

## Part I Basics

## 2. Thermodynamics and statistical mechanics

2.1 Classical thermodynamics	12
2.1.1 Auxiliary functions	18
2.1.2 Chemical potential and equilibrium	21
2.1.3 Energy, pressure, and chemical potential	23
2.2 Statistical thermodynamics	25
2.2.1 Basic assumption	25
2.2.2 Systems at constant temperature	27
2.2.3 Towards classical statistical mechanics	28
2.3 Ensembles	31
2.3.1 Micro-canonical (constant-NVE) ensemble	31
2.3.2 Canonical (constant-NVT) ensemble	32
2.3.3 Isobaric-isothermal (constant-NPT) ensemble	33
2.3.4 Grand-canonical (constant- $\mu$ VT) ensemble	34
2.4 Ergodicity	36
2.5 Linear response theory	38
2.5.1 Static response	39
2.5.2 Dynamic response	41
2.6 Questions and exercises	45

## 3. Monte Carlo simulations

3.1 Preamble: molecular simulations	53
3.2 The Monte Carlo method	54
3.2.1 Metropolis method	56
3.2.2 Parsimonious Metropolis algorithm	62
3.3 A basic Monte Carlo algorithm	62
3.3.1 The algorithm	62



3.3.2	Technical details	63
3.3.2.1	Boundary conditions	65
3.3.2.2	Truncation of interactions	67
3.3.2.3	Whenever possible, use potentials that need no truncation	72
3.3.2.4	Initialization	72
3.3.2.5	Reduced units	73
3.3.3	Detailed balance versus balance	78
3.4	Trial moves	81
3.4.1	Translational moves	81
3.4.2	Orientational moves	87
3.4.2.1	Rigid, linear molecules	88
3.4.2.2	Rigid, nonlinear molecules	88
3.4.2.3	Non-rigid molecules	89
3.5	Questions and exercises	92
4.	<b>Molecular Dynamics simulations</b>	
4.1	Molecular Dynamics: the idea	97
4.2	Molecular Dynamics: a program	98
4.2.1	Initialization	99
4.2.2	The force calculation	102
4.2.3	Integrating the equations of motion	104
4.3	Equations of motion	106
4.3.1	Accuracy of trajectories and the Lyapunov instability	106
4.3.2	Other desirable features of an algorithm	110
4.3.3	Other versions of the Verlet algorithm	112
4.3.4	Liouville formulation of time-reversible algorithms	118
4.3.5	One more way to look at the Verlet algorithm...	122
4.4	Questions and exercises	123
5.	<b>Computer experiments</b>	
5.1	Static properties	127
5.1.1	Temperature	127
5.1.2	Internal energy	128
5.1.3	Partial molar quantities	128
5.1.4	Heat capacity	129
5.1.5	Pressure	130
5.1.5.1	Pressure by thermodynamic integration	133
5.1.5.2	Local pressure and method of planes	133
5.1.5.3	Virtual volume changes	134
5.1.5.4	Compressibility	135
5.1.6	Surface tension	135
5.1.7	Structural properties	139
5.1.7.1	Structure factor	139
5.1.7.2	Radial distribution function	140
5.2	Dynamical properties	147
5.2.1	Diffusion	148



5.2.2	Order-n algorithm to measure correlations	155
5.2.3	Comments on the Green-Kubo relations	160
5.3	Statistical errors	167
5.3.1	Static properties: system size	167
5.3.2	Correlation functions	169
5.3.3	Block averages	171
5.4	Questions and exercises	174

## Part II

### Ensembles

#### 6. Monte Carlo simulations in various ensembles

6.1	General approach	182
6.2	Canonical ensemble	182
6.2.1	Monte Carlo simulations	183
6.2.2	Justification of the algorithm	183
6.3	Isobaric-isothermal ensemble	184
6.3.1	Statistical mechanical basis	184
6.3.2	Monte Carlo simulations	188
6.3.3	Applications	191
6.4	Isotension-isothermal ensemble	193
6.5	Grand-canonical ensemble	195
6.5.1	Statistical mechanical basis	196
6.5.2	Monte Carlo simulations	199
6.5.3	Molecular case	203
6.5.4	Semigrand ensemble	206
6.5.4.1	Phase coexistence in the semigrand ensemble	209
6.5.4.2	Chemical equilibria	211
6.6	Phase coexistence without boundaries	216
6.6.1	The Gibbs-ensemble technique	217
6.6.2	The partition function	218
6.6.3	Monte Carlo simulations	219
6.6.4	Applications	226
6.7	Questions and exercises	228

#### 7. Molecular Dynamics in various ensembles

7.1	Molecular Dynamics at constant temperature	234
7.1.1	Stochastic thermostats	237
7.1.1.1	Andersen thermostat	237
7.1.1.2	Local, momentum-conserving stochastic thermostat	239
7.1.1.3	Langevin dynamics	242
7.1.2	Global kinetic-energy rescaling	244
7.1.2.1	Extended Lagrangian approach	245
7.1.2.2	Application	253
7.1.3	Stochastic global energy rescaling	256



7.1.4	Choose your thermostat carefully	257
7.2	Molecular Dynamics at constant pressure	258
7.3	Questions and exercises	259

## Part III

## Free-energy calculations

### 8. Free-energy calculations

8.1	Introduction	263
8.1.1	Importance sampling may miss important states	263
8.1.2	Why is free energy special?	264
8.2	General note on free energies	267
8.3	Free energies and first-order phase transitions	267
8.3.1	Cases where free-energy calculations are not needed	268
8.3.1.1	Direct coexistence calculations	268
8.3.1.2	Coexistence without interfaces	270
8.3.1.3	Tracing coexistence curves	270
8.4	Methods to compute free energies	274
8.4.1	Thermodynamic integration	274
8.4.2	Hamiltonian thermodynamic integration	277
8.5	Chemical potentials	279
8.5.1	The particle insertion method	280
8.5.2	Particle-insertion method: other ensembles	284
8.5.3	Chemical potential differences	287
8.6	Histogram methods	288
8.6.1	Overlapping-distribution method	289
8.6.2	Perturbation expression	292
8.6.3	Acceptance-ratio method	293
8.6.4	Order parameters and Landau free energies	296
8.6.5	Biased sampling of free-energy profiles	299
8.6.6	Umbrella sampling	301
8.6.7	Density-of-states sampling	303
8.6.8	Wang-Landau sampling	304
8.6.9	Metadynamics	309
8.6.10	Piecing free-energy profiles together: general aspects	311
8.6.11	Piecing free-energy profiles together: MBAR	312
8.7	Non-equilibrium free energy methods	317
8.8	Questions and exercises	320

### 9. Free energies of solids

9.1	Thermodynamic integration	324
9.2	Computation of free energies of solids	326
9.2.1	Atomic solids with continuous potentials	326
9.2.2	Atomic solids with discontinuous potentials	329
9.2.3	Molecular and multi-component crystals	330
9.2.4	Einstein-crystal implementation issues	332



9.2.5	Constraints and finite-size effects	340
9.3	<b>Vacancies and interstitials</b>	346
9.3.1	Defect free energies	346
9.3.1.1	Vacancies	348
9.3.1.2	Interstitials	350

## 10. Free energy of chain molecules

10.1	Chemical potential as reversible work	351
10.2	<b>Rosenbluth sampling</b>	352
10.2.1	Macromolecules with discrete conformations	353
10.2.2	Extension to continuously deformable molecules	357
10.2.3	Overlapping-distribution Rosenbluth method	363
10.2.4	Recursive sampling	365
10.2.5	Pruned-enriched Rosenbluth method	366

## Part IV

## Advanced techniques

### 11. Long-ranged interactions

11.1	Introduction	371
11.2	<b>Ewald method</b>	373
11.2.1	Dipolar particles	382
11.2.2	Boundary conditions	385
11.2.3	Accuracy and computational complexity	386
11.3	<b>Particle-mesh approaches</b>	388
11.4	<b>Damped truncation</b>	393
11.5	<b>Fast-multipole methods</b>	394
11.6	<b>Methods that are suited for Monte Carlo simulations</b>	398
11.6.1	Maxwell equations on a lattice	399
11.6.2	Event-driven Monte Carlo approach	402
11.7	<b>Hyper-sphere approach</b>	402

### 12. Configurational-bias Monte Carlo

12.1	<b>Biased sampling techniques</b>	406
12.1.1	Beyond Metropolis	406
12.1.2	Orientational bias	407
12.2	<b>Chain molecules</b>	413
12.2.1	Configurational-bias Monte Carlo	414
12.2.2	Lattice models	414
12.2.3	Off-lattice case	417
12.3	<b>Generation of trial orientations</b>	424
12.3.1	Strong intramolecular interactions	424
12.4	<b>Fixed endpoints</b>	432
12.4.1	Lattice models	432
12.4.2	Fully flexible chain	434



12.4.3 Strong intramolecular interactions	436
12.5 Beyond polymers	436
12.6 Other ensembles	440
12.6.1 Grand-canonical ensemble	440
12.7 Recoil growth	445
12.7.1 Algorithm	446
12.8 Questions and exercises	450
<b>13. Accelerating Monte Carlo sampling</b>	
13.1 Sampling intensive variables	455
13.1.1 Parallel tempering	457
13.1.2 Expanded ensembles	464
13.2 Noise on noise	467
13.3 Rejection-free Monte Carlo	468
13.3.1 Hybrid Monte Carlo	468
13.3.2 Kinetic Monte Carlo	469
13.3.3 Sampling rejected moves	471
13.4 Enhanced sampling by mapping	473
13.4.1 Machine learning and the rebirth of static Monte Carlo sampling	475
13.4.2 Cluster moves	479
13.4.2.1 Cluster moves on lattices	480
13.4.2.2 Off-lattice cluster moves	482
13.4.3 Early rejection method	484
13.4.4 Beyond detailed-balance	486
<b>14. Time-scale-separation problems in MD</b>	
14.1 Constraints	494
14.1.1 Constrained and unconstrained averages	499
14.1.2 Beyond bond constraints	505
14.2 On-the-fly optimization	506
14.3 Multiple time-step approach	509
<b>15. Rare events</b>	
15.1 Theoretical background	516
15.2 Bennett-Chandler approach	520
15.2.1 Dealing with holonomic constraints (Blue-Moon ensemble)	522
15.3 Diffusive barrier crossing	527
15.4 Path-sampling techniques	534
15.4.1 Transition-path sampling	535
15.4.1.1 Path ensemble	536
15.4.1.2 Computing rates	538
15.4.2 Path sampling Monte Carlo	543
15.4.3 Beyond transition-path sampling	546
15.4.4 Transition-interface sampling	546
15.5 Forward-flux sampling	547



15.5.1 Jumpy forward-flux sampling	548
15.5.2 Transition-path theory	549
15.5.3 Mean first-passage times	552
15.6 Searching for the saddle point	556
15.7 Epilogue	558

## 16. Mesoscopic fluid models

16.1 Dissipative-particle dynamics	561
16.1.1 DPD implementation	562
16.1.2 Smoothed dissipative-particle dynamics	566
16.2 Multi-particle collision dynamics	567
16.3 Lattice-Boltzmann method	569

## Part V

## Appendices

A. Lagrangian and Hamiltonian equations of motion	573
A.1 Action	573
A.2 Lagrangian	575
A.3 Hamiltonian	577
A.4 Hamilton dynamics and statistical mechanics	580
A.4.1 Canonical transformation	580
A.4.2 Symplectic condition	581
A.4.3 Statistical mechanics	583
B. Non-Hamiltonian dynamics	587
C. Kirkwood-Buff relations	591
C.1 Structure factor for mixtures	591
C.2 Kirkwood-Buff in simulations	593
D. Non-equilibrium thermodynamics	595
D.1 Entropy production	595
D.1.1 Enthalpy fluxes	597
D.2 Fluctuations	597
D.3 Onsager reciprocal relations	600
E. Non-equilibrium work and detailed balance	603
F. Linear response: examples	607
F.1 Dissipation	607
F.2 Electrical conductivity	610
F.3 Viscosity	611
F.4 Elastic constants	612



<b>G.</b>	<b>Committor for 1d diffusive barrier crossing</b>	617
G.1	1d diffusive barrier crossing	617
G.2	Computing the committor	618
<b>H.</b>	<b>Smoothed dissipative particle dynamics</b>	621
H.1	Navier-Stokes equation and Fourier's law	621
H.2	Discretized SDPD equations	622
<b>I.</b>	<b>Saving CPU time</b>	625
I.1	Verlet list	625
I.2	Cell lists	629
I.3	Combining the Verlet and cell lists	630
I.4	Efficiency	631
<b>J.</b>	<b>Some general purpose algorithms</b>	637
J.1	Gaussian distribution	637
J.2	Selection of trial orientations	638
J.3	Generate random vector on a sphere	638
J.4	Generate bond length	639
J.5	Generate bond angle	640
J.6	Generate bond and torsion angle	641
 <b>Part VI</b>		
<b>Repository<sup>1</sup></b>		
<b>K.</b>	<b>Errata</b>	645
<b>L.</b>	<b>Miscellaneous methods</b>	647
<b>M.</b>	<b>Miscellaneous examples</b>	649
<b>N.</b>	<b>Supporting information for case studies</b>	651
<b>O.</b>	<b>Small research projects</b>	653
<b>P.</b>	<b>Hints for programming</b>	655
Bibliography		657
Acronyms		695
Glossary		697
Index		701
Author index		715

<sup>1</sup> Repository is available in its entirety online at <https://www.elsevier.com/books-and-journals/book-companion/9780323902922>.



# Online appendices

K. Errata	e1
L. Miscellaneous methods	e3
L.1 Higher-order integration schemes	e3
L.2 Surface tension via the pressure tensor	e4
L.3 Micro-canonical Monte Carlo	e5
L.4 Details of the Gibbs “ensemble”	e6
L.4.1 Free energy of the Gibbs ensemble	e6
L.4.1.1 Basic definitions and results for the canonical ensemble	e6
L.4.1.2 The free energy density in the Gibbs ensemble	e8
L.4.2 Graphical analysis of simulation results	e13
L.4.3 Chemical potential in the Gibbs ensemble	e17
L.4.4 Algorithms of the Gibbs ensemble	e18
L.5 Multi-canonical ensemble method	e18
L.6 Nosé-Hoover dynamics	e22
L.6.1 Nosé-Hoover dynamics equations of motion	e22
L.6.1.1 The Nosé-Hoover algorithm	e22
L.6.1.2 Nosé-Hoover chains	e24
L.6.1.3 The NPT ensemble	e30
L.6.2 Nosé-Hoover algorithms	e32
L.6.2.1 Canonical ensemble	e33
L.6.2.2 The isothermal-isobaric ensemble	e37
L.7 Ewald summation in a slab geometry	e41
L.8 Special configurational-bias Monte Carlo cases	e45
L.8.1 Generation of branched molecules	e45
L.8.2 Rebridging Monte Carlo	e48
L.8.3 Gibbs-ensemble simulations	e50
L.9 Recoil growth: justification of the method	e54
L.10 Overlapping distribution for polymers	e57
L.11 Hybrid Monte Carlo	e61
L.12 General cluster moves	e62
L.13 Boltzmann-sampling with dissipative particle dynamics	e65
L.14 Reference states	e67
L.14.1 Grand-canonical ensemble simulation	e67
L.14.1.1 Preliminaries	e67
L.14.1.2 Ideal gas	e68
L.14.1.3 Grand-canonical simulations	e68
M. Miscellaneous examples	e71
M.1 Gibbs ensemble for dense liquids	e71
M.2 Free energy of a nitrogen crystal	e71
M.3 Zeolite structure solution	e74



<b>N.</b>	<b>Supporting information for case studies</b>	<b>e75</b>
N.1	Equation of state of the Lennard-Jones fluid-I	e75
N.2	Importance of detailed balance	e77
N.3	Why count the old configuration again?	e79
N.4	Static properties of the Lennard-Jones fluid	e79
N.5	Dynamic properties of the Lennard-Jones fluid	e82
N.6	Algorithms to calculate the mean-squared displacement	e83
N.7	Equation of state of the Lennard-Jones fluid	e85
N.8	Phase equilibria from constant-pressure simulations	e86
N.9	Equation of state of the Lennard-Jones fluid - II	e87
N.10	Phase equilibria of the Lennard-Jones fluid	e87
N.11	Use of Andersen thermostat	e89
N.12	Use of Nosé-Hoover thermostat	e90
N.13	Harmonic oscillator (I)	e92
N.14	Nosé-Hoover chain for harmonic oscillator	e93
N.15	Chemical potential: particle-insertion method	e93
N.16	Chemical potential: overlapping distributions	e94
N.17	Solid-liquid equilibrium of hard spheres	e96
N.18	Equation of state of Lennard-Jones chains	e101
N.19	Generation of trial configurations of ideal chains	e101
N.20	Recoil growth simulation of Lennard-Jones chains	e104
N.21	Multiple time step versus constraints	e107
N.22	Ideal gas particle over a barrier	e109
N.23	Single particle in a two-dimensional potential well	e112
N.24	Dissipative particle dynamics	e114
N.25	Comparison of schemes for the Lennard-Jones fluid	e116
<b>O.</b>	<b>Small research projects</b>	<b>e119</b>
O.1	Adsorption in porous media	e119
O.2	Transport properties of liquids	e120
O.3	Diffusion in a porous medium	e120
O.4	Multiple-time-step integrators	e121
O.5	Thermodynamic integration	e122
<b>P.</b>	<b>Hints for programming</b>	<b>e125</b>