

CONTENTS

LIST OF SYMBOLS	x v
1 INTRODUCTION	1
1.1 A short history of computer simulation	1
1.2 Computer simulation: motivation and applications	4
1.3 Model systems and interaction potentials	6
1.3.1 Introduction	6
1.3.2 Atomic systems	7
1.3.3 Molecular systems	12
1.3.4 Lattice systems	16
1.3.5 Calculating the potential	18
1.4 Constructing an intermolecular potential	20
1.4.1 Introduction	20
1.4.2 Building the model potential	20
1.4.3 Adjusting the model potential	22
1.5 Studying small systems	23
1.5.1 Introduction	23
1.5.2 Periodic boundary conditions	24
1.5.3 Potential truncation	27
1.5.4 Computer code for periodic boundaries	29
1.5.5 Spherical boundary conditions	32
2 STATISTICAL MECHANICS	33
2.1 Sampling from ensembles	33
2.2 Common statistical ensembles	39
2.3 Transforming between ensembles	43
2.4 Simple thermodynamic averages	46
2.5 Fluctuations	51
2.6 Structural quantities	54
2.7 Time correlation functions and transport coefficients	58
2.8 Long-range corrections	64
2.9 Quantum corrections	65
2.10 Constraints	68
3 MOLECULAR DYNAMICS	71
3.1 Equations of motion for atomic systems	71
3.2 Finite difference methods	73
3.2.1 The Verlet algorithm	78
3.2.2 The Gear predictor-corrector	82
3.2.3 Other methods	84
3.3 Molecular dynamics of rigid non-spherical bodies	84
3.3.1 Non-linear molecules	85
3.3.2 Linear molecules	90

CONTENTS

3.4 Constraint dynamics	92
3.5 Checks on accuracy	98
3.6 Molecular dynamics of hard systems	101
3.6.1 Hard spheres	102
3.6.2 Hard non-spherical bodies	108
4 MONTE CARLO METHODS	110
4.1 Introduction	110
4.2 Monte Carlo integration	111
4.2.1 Hit and miss	111
4.2.2 Sample mean integration	112
4.3 Importance sampling	114
4.4 The Metropolis method	118
4.5 Isothermal-isobaric Monte Carlo	123
4.6 Grand canonical Monte Carlo	126
4.7 Molecular liquids	131
4.7.1 Rigid molecules	131
4.7.2 Non-rigid molecules	135
5 SOME TRICKS OF THE TRADE	140
5.1 Introduction	140
5.2 The heart of the matter	140
5.2.1 Efficient calculation of forces, energies, and pressures	140
5.2.2 Avoiding the square root	143
5.2.3 Table look-up and spline-fit potentials	143
5.2.4 Shifted and shifted-force potentials	145
5.3 Neighbour lists	146
5.3.1 The Verlet neighbour list	147
5.3.2 Cell structures and linked lists	149
5.4 Multiple time step methods	152
5.5 How to handle long-range forces	155
5.5.1 Introduction	155
5.5.2 The Ewald sum	156
5.5.3 The reaction field method	162
5.5.4 Other methods	164
5.5.5 Summary	164
5.6 When the dust has settled	166
5.7 Starting up	168
5.7.1 The initial configuration	168
5.7.2 The initial velocities	170
5.7.3 Equilibration	171
5.8 Organization of the simulation	173
5.8.1 Input/output and file handling	174
5.8.2 Program structure	175
5.8.3 The scheme in action	180
6 HOW TO ANALYSE THE RESULTS	182
6.1 Introduction	182
6.2 Liquid structure	183

CONTENTS

xi

6.3		185
6.3.1	The direct approach	185
6.3.2	The fast Fourier transform method	188
6.4		191
6.4.1	Errors in equilibrium averages	192
6.4.2	Errors in fluctuations	195
6.4.3	Errors in structural quantities	195
6.4.4	Errors in time correlation functions	196
6.5		198
6.5.1	Correcting thermodynamic averages	199
6.5.2	Extending $g(r)$ to large r	199
6.5.3	Extrapolating $g(r)$ to contact	201
6.5.4	Smoothing $g(r)$	203
6.5.5	Calculating transport coefficients	204
6.5.6	Smoothing a spectrum	208
7	AI	212
7.1	Introduction	212
7.2		213
7.2.1	7.2. I Introduction	213
7.2.2	Non-Boltzmann sampling	213
7.2.3	Acceptance ratio method	218
7.2.4	Summary	219
7.3		220
7.3.1	7.3.1 Preferential sampling	220
7.3.2	7.3.2 Force-bias Monte Carlo	224
7.3.3	7.3.3 Smart Monte Carlo	225
7.3.4	7.3.4 Virial-bias Monte Carlo	226
7.		227
7.4.1	7.4. 1 Stochastic methods	227
7.4.2	7.4.2 Extended system methods	228
7.4.3	7.4.3 Constraint methods	230
7.4.4	7.4.4 Other methods	231
7.		232
7.5.1	7.5. 1 Extended system methods	232
7.5.2	7.5.2 Constraint methods	234
7.5.3	7.5.3 Other methods	236
7.5.4	7.5.4 Changing box shape	236
7.	Practical points	238
7.		239
8	N	240
8.1	Introduction	240
8.1	Shear flow	242
8		249
8	Heat flow	250
8	Diffusion	251
8	Other perturbations	253
8	Practical points	253

9 BROWNIAN DYNAMICS	257
9.1 Introduction	257
9.2 Projection operators	257
9.3 Brownian dynamics	259
9.4 Hydrodynamic and memory effects	264
10 QUANTUM SIMULATIONS	270
10.1 Introduction	270
10.2 Semiclassical path-integral simulations	272
10.3 Semiclassical Gaussian wavepackets	279
10.4 Quantum random walk simulations	282
11 SOME APPLICATIONS	286
11.1 Introduction	286
11.2 The liquid drop	286
11.3 Melting	292
11.4 Molten salts	298
11.5 Liquid crystals	300
11.6 Rotational dynamics	306
11.7 Long-time tails	310
11.8 Interfaces	312
APPENDIX A COMPUTERS AND COMPUTER SIMULATION	320
A.1 Computer hardware	320
A.2 Programming languages	322
A.3 Efficient programming in FORTRAN-77	324
APPENDIX B REDUCED UNITS	327
B.1 Reduced units	327
APPENDIX C CALCULATION OF FORCES AND TORQUES	329
C.1 Introduction	329
C.2 The polymer chain	329
C.3 The molecular fluid with multipoles	332
C.4 The triple-dipole potential	334
APPENDIX D FOURIER TRANSFORMS	336
D.1 The Fourier transform	336
D.2 The discrete Fourier transform	337
D.3 Numerical Fourier transforms	338
APPENDIX E THE GEAR PREDICTOR-CORRECTOR	340
E.1 The Gear predictor-corrector	340
APPENDIX F PROGRAM AVAILABILITY	343

APPENDIX G RANDOM NUMBERS	345
G.1 Random number generators	345
G.2 Random numbers uniform on $(0,1)$	345
G.3 Generating non-uniform distributions	347
G.4 Random vectors on the surface of a sphere	349
G.5 Choosing randomly and uniformly from complicated regions	349
G.6 Sampling from an arbitrary distribution	351
REFERENCES	352
INDEX	383