

Ruben Santamaria

Molecular Dynamics

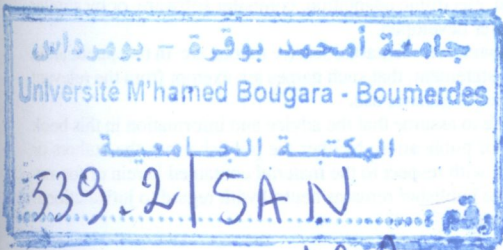
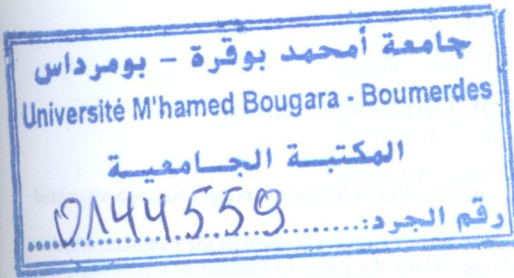


Springer



Ruben Santamaria

Molecular Dynamics



Springer

Contents

Part I Basics of Classical Mechanics

1 Principles of Classical Dynamics	3
1.1 Newtonian Dynamics	3
1.2 Space and Time	4
1.3 Mass	5
1.4 Energy	8
1.5 Electric Charge	9
1.6 Reference System of Coordinates	11
1.7 Newtonian Time	12
1.8 Linear Motion	13
1.9 Angular Motion	16
1.10 Descriptions Between Inertial Reference Frames	19
References	22
2 Foundations of Newtonian Dynamics	23
2.1 First Newton's Law	23
2.2 Second Newton's Law	26
2.3 Third Newton's Law	29
2.4 Reduced Mass of a Two-Particle System	30
2.5 Time Reversibility	30
2.6 Angular Momentum and Torque	33
2.7 Impulse, Work, and Power	34
2.8 Kinetic and Potential Energies	36
2.9 Energy Conservation	38
References	40
3 Many-Particle Systems	41
3.1 Reference Frame of a Many-Particle System	41
3.2 Angular Momentum and Torque of a Many-Particle System	43
3.3 Mechanical Energies of a Many-Particle System	44
3.4 Transformation of the Energy Components	47
3.5 Energy Balance Equation	48
3.6 Statistical and Time Averages of Physical Observables	50
3.7 Ergodic Hypothesis	52

3.8	Breaking the Ergodic Hypothesis	56
3.9	Velocity Distribution Function	56
3.10	Temperature of a System of Particles	57
3.11	Temperature Scaling as a Thermostat	60
3.12	Temperature Fluctuations	61
3.13	Pressure and Volume	63
3.14	The Virial and the Equation of State	65
	References	68
4	Mechanical Descriptors	69
4.1	Caloric Curve	69
4.2	Interatomic Distance Fluctuations	70
4.3	Root Mean Square Deviation of Positions	71
4.4	Orientational Order Parameter	71
4.5	Probability Distribution Functions	72
4.6	Correlation Functions	75
4.7	Properties of Correlation Functions	78
4.8	Vibrational Spectra from Autocorrelation Functions	81
	References	82
5	Rigid Body	85
5.1	Angular Momentum of a Rotating System of Particles	85
5.2	External Torques Acting on a Rotating Body	89
5.3	Total Energy of a Rotating Rigid Body	91
A.1	Appendix: Matrix Diagonalization	93
6	Analytical Mechanics	97
6.1	Action Function	98
6.2	Principle of Stationary Action	99
6.3	Classifying Molecular Systems	101
6.4	Lagrange's Equations of Motion	103
6.5	Newtonian Equations of Motion from Lagrange Theory	107
6.6	Non-uniqueness of the Lagrangian	108
6.7	Invariance of the Lagrange Equations of Motion	111
6.8	Motion with Constraints	112
6.9	Hamilton's Function	117
6.10	Preservation of the Hamiltonian in Time	119
6.11	Conserved Observables and Symmetries	121
6.12	Space Homogeneity	124
6.13	Space Isotropy	125
6.14	Uniform Passage of Time	125
6.15	Hamilton's Equations of Motion	127
6.16	Invariance Under Canonical Transformations	129
6.17	Time Reversibility in Hamiltonian Theory	132
6.18	Hamilton-Jacobi Theory	134
6.19	Illustrating with the Harmonic Oscillator	137

6.20	Contact Between Quantum and Classical Mechanics	138
6.21	Poisson's Brackets	140
6.22	Classical Time Propagator	143
	References	146

Part II Basics of Quantum Mechanics

7	Wave-Particle Duality of Matter	149
7.1	Young's Experiment	149
7.2	Interference of Waves	150
7.3	Photo-Electron Experiment	151
7.4	Compton's Experiment	154
7.5	Davission-Germer's Experiment	155
7.6	de Broglie's Hypothesis	155
7.7	Bohr's Complementary Principle	157
	References	157
8	Quantization of the Energy	159
8.1	Planck's Energy Equation	159
8.2	Blackbody Radiation Experiment	160
8.3	Rayleigh-Jeans Law	161
8.4	Wien's Displacement Law	162
8.5	Ultraviolet Catastrophe	163
8.6	Planck's Law	163
8.7	Franck-Hertz Experiment	165
8.8	Heisenberg's Uncertainty Principle	167
A.1	Appendix: Planck's Radiation Intensity Law	170
A.1.1	Average Energy	171
A.1.2	Density of States	172
A.1.3	Energy per Volume per Frequency	173
A.1.4	Irradiance	175
A.1.5	Maximum Intensity	176
A.1.6	Time Interval of Temperature Cooling	177
	Reference	178
9	Quantization of the Angular Momentum	179
9.1	Orbital Angular Momentum and Spin	179
9.2	Characterizing a Particle with Spin	181
9.3	Stern-Gerlach Experiment	182
9.4	Wave-Particle Duality and Spin of a Particle	185
9.5	Fermions and Bosons	186
9.6	Pauli's Exclusion Principle and Hund's Rule	186
A.1	Appendix: Magnetic Moment	188
A.1.1	Electric Current in a Circular Loop	188
A.1.2	Magnetic g Factor	190
A.1.3	Magnetic Energy and Magnetic Work	191

A.1.4	Zeeman Effect	193
A.1.5	Electron Spin	196
A.1.6	Paschen-Back Effect	198
A.1.7	Applications of the Spin Resonance Technique	199
B.1	Appendix: Spin Functions and Operators.....	200
References		204
10	Postulates of Quantum Mechanics	205
10.1	Reformulating the Conceptual World	206
10.2	Postulates of Quantum Mechanics	207
10.2.1	First Postulate	207
10.2.2	Second Postulate	208
10.2.3	Third Postulate	210
10.2.4	Fourth Postulate	210
10.2.5	Fifth Postulate	213
10.2.6	Sixth Postulate.....	214
10.3	Time Reversibility in Quantum Mechanics	215
10.4	Stationary States	219
10.5	Superposition Principle of Quantum States.....	221
10.6	Bohr's Correspondence Principle	222
10.7	Selection Rules.....	224
10.8	Pauli's Principle in the Electronic Wave Function	228
10.9	Wave Function of the Electrons in a Molecule	229
10.10	Variational Principle of the Energy	233
A.1	Appendix: Proposing the Wave Equation for Matter Waves	235
B.1	Appendix: Expansion of a Determinantal Wave Function	237
References		240
 Part III First-Principles Molecular Dynamics		
11	Dynamics of Electrons and Nuclei	243
11.1	The Electronic and Nuclear Dynamics Are Coupled.....	244
11.2	Molecular Hamiltonian	244
11.3	Approximating the Total Wave Function	246
11.4	Time-Dependent Self-Consistent Field Equations	250
References		253
12	Classical Limit of the Nuclear Motion	255
12.1	Polar Form of the Nuclear Wave Equation	256
12.2	Continuity and Hamilton-Jacobi Equations	259
12.3	Conditions to Describe the Nuclear Particles Classically	263
12.4	Simplification of the Nuclear Potential	267
12.5	Parameterizing the Potential Function	271
12.6	Total Energy of the Molecular System.....	274
12.7	Establishing the Accuracy of Atomic Forces	277
12.8	Diffusion from the Continuity Equation	278

12.9	Diffusion Equation and Particle Flux	279
12.10	Expansion of the Electronic Wave Equation	283
12.11	Expansion of the Newtonian Equation of the Nuclei	286
A.1	Appendix: Bohm's Quantum Potential	288
	References	290

Part IV Classical Molecular Dynamics

13	Classical Molecular Dynamics	295
13.1	Model Interaction Potentials	296
13.2	Forcefields	298
13.3	Atom Types	299
13.4	United Atom	300
13.5	Bond Elongation and Compression	300
13.6	Combination Rules	302
13.7	Bond Angle Vibration	303
13.8	Plane Bending	304
13.9	Angle Inversion	305
13.10	Torsional Motion	306
13.11	Electrostatic Interaction	307
13.12	van der Waals Forces	308
13.13	Interaction Potential Functions of Water	311
13.14	Atom Polarization	312
13.15	External Fields and Potentials	314
13.16	Parameterization of Forcefields	315
13.17	Model Potentials of Non-biological Systems	317
13.18	Sutton-Chen Potential Function	318
13.19	Gupta Potential Function	319
13.20	Tersoff Potential Function	320
A.1	Appendix: Harmonic Model of the Dispersion Energy	322
	References	325
14	Extended Systems	327
14.1	Fixed and Flexible Boundaries	328
14.2	Periodic Boundary Conditions	330
14.3	The <i>PBC</i> System Is an Open System	334
14.4	Electrostatics in the <i>PBC</i> Approach	336
14.5	Ewald Sum Approach	337
14.6	Using the Poisson Equation	339
14.7	Short-Range Interactions	343
14.8	Electrostatic Self-Interactions	344
14.9	Long-Range Interactions	344
14.10	Ewald Electrostatic Energy	348
14.11	Smooth Particle Mesh Ewald Approach	350
14.12	Shifted Potentials and Forces	352
	References	356

Part V Time Evolution Operators

15 Integrating the Equations of Motion	359
15.1 Liouville Operator as a Time Propagator	359
15.2 Discretizing the Time Propagator	361
15.3 Evolving Positions and Momenta	363
15.4 Simplified Time Integrators	367
15.5 Leapfrog Algorithm	368
15.6 Verlet Algorithm	370
15.7 Bond Constraints	373
References	376
Index	379