

# Contents

## Part I Statistical Mechanics of Biopolymers

<b>1</b>	<b>Random Walk Models for the Conformation</b>	3
1.1	The Freely Jointed Chain	3
1.1.1	Entropic Elasticity	5
1.1.2	Force–Extension Relation	6
1.2	Two Component Model	9
1.2.1	Force-Extension Relation	10
1.2.2	Two Component Model with Interactions	12
<b>2</b>	<b>Flory–Huggins Theory for Biopolymer Solutions</b>	21
2.1	Monomeric Solution	21
2.2	Polymeric Solution	24
2.3	Phase Transitions	30
2.3.1	Stability Criterion	30
2.3.2	Critical Coupling	32
2.3.3	Phase Diagram	34
	Problems	37

## Part II Protein Electrostatics and Solvation

<b>3</b>	<b>Implicit Continuum Solvent Models</b>	41
3.1	Potential of Mean Force	41
3.2	Dielectric Continuum Model	42
3.3	Born Model	44
3.4	Charges in a Protein	45
3.5	Time Dependent Reaction Field	48
3.6	Generalized Born Models	50

<b>4</b>	<b>Debye–Hückel Theory</b> . . . . .	53
4.1	Electrostatic Shielding by Mobile Charges . . . . .	53
4.2	1-1 Electrolytes . . . . .	55
4.3	Charged Sphere . . . . .	55
4.4	Charged Cylinder . . . . .	58
4.5	Charged Membrane (Göy–Chapman Double Layer) . . . . .	61
4.6	Stern Modification of the Double Layer . . . . .	67
	Problems . . . . .	68
<b>5</b>	<b>Protonation Equilibria</b> . . . . .	71
5.1	Protonation Equilibria in Solution . . . . .	71
5.2	Protonation Equilibria in Proteins . . . . .	75
5.2.1	Apparent $pK_a$ Values . . . . .	75
5.2.2	Protonation Enthalpy . . . . .	76
5.2.3	Protonation Enthalpy Relative to the Uncharged State . . . . .	78
5.2.4	Statistical Mechanics of Protonation . . . . .	79
5.3	Abnormal Titration Curves of Coupled Residues . . . . .	80
	Problems . . . . .	81
<b>Part III Reaction Kinetics</b>		
<b>6</b>	<b>Formal Kinetics</b> . . . . .	85
6.1	Elementary Chemical Reactions . . . . .	85
6.2	Reaction Variable and Reaction Rate . . . . .	85
6.3	Reaction Order . . . . .	87
6.3.1	Zero-Order Reactions . . . . .	87
6.3.2	First-Order Reactions . . . . .	87
6.3.3	Second-Order Reactions . . . . .	88
6.4	Dynamical Equilibrium . . . . .	89
6.5	Competing Reactions . . . . .	90
6.6	Consecutive Reactions . . . . .	90
6.7	Enzymatic Catalysis . . . . .	91
6.8	Reactions in Solutions . . . . .	93
6.8.1	Diffusion Controlled Limit . . . . .	94
6.8.2	Reaction Controlled Limit . . . . .	95
	Problems . . . . .	95
<b>7</b>	<b>Kinetic Theory – Fokker-Planck Equation</b> . . . . .	97
7.1	Stochastic Differential Equation for Brownian Motion . . . . .	97
7.2	Probability Distribution . . . . .	99
7.3	Diffusion . . . . .	101
7.3.1	Sharp Initial Distribution . . . . .	102
7.3.2	Absorbing Boundary . . . . .	103

7.4	Fokker–Planck Equation for Brownian Motion . . . . .	104
7.5	Stationary Solution to the Fokker–Planck Equation . . . . .	105
7.6	Diffusion in an External Potential . . . . .	107
7.7	Large Friction Limit – Smoluchowski Equation . . . . .	109
7.8	Master Equation . . . . .	110
	Problems . . . . .	110
<b>8</b>	<b>Kramers Theory</b> . . . . .	<b>113</b>
8.1	Kramers’ Model . . . . .	113
8.2	Kramers’ Calculation of the Reaction Rate . . . . .	115
<b>9</b>	<b>Dispersive Kinetics</b> . . . . .	<b>119</b>
9.1	Dichotomous Model . . . . .	120
9.1.1	Fast Solvent Fluctuations . . . . .	123
9.1.2	Slow Solvent Fluctuations . . . . .	124
9.1.3	Numerical Example . . . . .	125
9.2	Continuous Time Random Walk Processes . . . . .	126
9.2.1	Formulation of the Model . . . . .	126
9.2.2	Exponential Waiting Time Distribution . . . . .	127
9.2.3	Coupled Equations . . . . .	129
9.3	Powertime Law Kinetics . . . . .	134
	Problems . . . . .	136
 <b>Part IV Transport Processes</b>		
<b>10</b>	<b>Non-equilibrium Thermodynamics</b> . . . . .	<b>139</b>
10.1	Continuity Equation for the Mass Density . . . . .	140
10.2	Energy Conservation . . . . .	141
10.3	Entropy Production . . . . .	142
10.4	Phenomenological Relations . . . . .	145
10.5	Stationary States . . . . .	145
	Problems . . . . .	147
<b>11</b>	<b>Simple Transport Processes</b> . . . . .	<b>149</b>
11.1	Heat Transport . . . . .	149
11.2	Diffusion in an External Electric Field . . . . .	150
	Problems . . . . .	153
<b>12</b>	<b>Ion Transport Through a Membrane</b> . . . . .	<b>155</b>
12.1	Diffusive Transport . . . . .	155
12.2	Goldman–Hodgkin–Katz Model . . . . .	158
12.3	Hodgkin–Huxley Model . . . . .	161
12.4	Cooperativity in Ion Channel Kinetics . . . . .	163
12.4.1	MWC Model . . . . .	164
12.4.2	KNF Model . . . . .	167

<b>13</b>	<b>Reaction–Diffusion Systems</b>	173
13.1	Derivation	173
13.2	Linearization	174
13.3	Fitzhugh–Nagumo Model	175

## Part V Reaction Rate Theory

<b>14</b>	<b>Equilibrium Reactions</b>	183
14.1	Arrhenius Law	183
14.2	Statistical Interpretation of the Equilibrium Constant	185
<b>15</b>	<b>Calculation of Reaction Rates</b>	187
15.1	Collision Theory	187
15.2	Transition State Theory	190
15.3	Comparison Between Collision Theory and Transition State Theory	192
15.4	Thermodynamical Formulation of TST	194
15.5	Kinetic Isotope Effects	195
15.6	General Rate Expressions	196
15.6.1	The Flux Operator	197
	Problems	199
<b>16</b>	<b>Marcus Theory of Electron Transfer</b>	201
16.1	Phenomenological Description of ET	201
16.2	Simple Explanation of Marcus Theory	204
16.3	Free Energy Contribution of the Nonequilibrium Polarization	205
16.4	Activation Energy	209
16.5	Simple Model Systems	213
16.5.1	Charge Separation	215
16.5.2	Charge Shift	216
16.6	The Energy Gap as the Reaction Coordinate	216
16.7	Inner Shell Reorganization	218
16.8	The Transmission Coefficient for Nonadiabatic Electron Transfer	219
16.9	Charge Delocalization and Self-Trapping	220
	Problems	223

## Part VI Elementary Photophysics

<b>17</b>	<b>Molecular States</b>	227
17.1	Born–Oppenheimer Separation	227
17.2	Harmonic Approximation to the Nuclear Motion	229
17.3	Nonadiabatic Interaction	232
17.4	“True” Molecular Eigenstates	235

<b>18</b>	<b>Intramolecular Electronic Transitions</b> . . . . .	237
18.1	Coupling to the Radiation Field . . . . .	238
18.2	Optical Transitions . . . . .	242
18.3	Dipole Transitions in the Condon Approximation. . . . .	244
18.4	Time-Correlation Function (TCF) Formalism . . . . .	245
18.5	Excitation by a Short Pulse. . . . .	246
18.6	Radiationless Transitions. . . . .	247
	18.6.1 Internal Conversion . . . . .	248
	18.6.2 Intersystem Crossing . . . . .	249
	Problems. . . . .	249
<b>19</b>	<b>The Displaced Harmonic Oscillator</b> . . . . .	251
19.1	The Time-Correlation Function in the Displaced Harmonic Oscillator Approximation . . . . .	251
19.2	High Frequency Modes. . . . .	254
19.3	Low Frequency Modes . . . . .	255
<b>20</b>	<b>Spectral Diffusion</b> . . . . .	257
20.1	Dephasing. . . . .	257
20.2	Gaussian Fluctuations . . . . .	260
	20.2.1 Long Correlation Time . . . . .	262
	20.2.2 Short Correlation Time . . . . .	262
20.3	Markovian Modulation . . . . .	263
	Problems. . . . .	267
<b>21</b>	<b>Crossing of Two Electronic States</b> . . . . .	269
21.1	Wavepacket Motion . . . . .	269
	21.1.1 Free Particle Motion . . . . .	270
	21.1.2 Harmonic Oscillator. . . . .	272
21.2	The Adiabatic to Diabatic Transformation . . . . .	273
21.3	Quasidiabatic States . . . . .	278
21.4	Crossing Between Two States. . . . .	280
21.5	Avoided Crossing Along One Coordinate. . . . .	281
21.6	Semiclassical Approximation . . . . .	284
21.7	Landau–Zener Model . . . . .	285
21.8	Application to Diabatic ET. . . . .	287
21.9	Conical Intersections. . . . .	288
21.10	Linear Vibronic Coupling Model . . . . .	290
	Problems. . . . .	293
<b>22</b>	<b>Dynamics of an Excited State</b> . . . . .	295
22.1	Coupling to a Quasi-continuum . . . . .	295
22.2	Green's Formalism . . . . .	296
	22.2.1 Resolvent and Propagator . . . . .	297
	22.2.2 Dyson Equation. . . . .	300

22.2.3	Transition Operator . . . . .	301
22.2.4	Level Shift . . . . .	301
22.3	Ladder Model . . . . .	303
22.4	Description Within the Saddle Point Method . . . . .	308
22.5	The Energy Gap Law . . . . .	313
	Problems . . . . .	317

## Part VII Elementary Photoinduced Processes

<b>23</b>	<b>Photophysics of Chlorophylls and Carotenoids . . . . .</b>	<b>321</b>
23.1	MO Model for the Electronic States . . . . .	321
23.2	The Free Electron Model for Polyenes . . . . .	322
23.3	The LCAO Approximation . . . . .	324
23.4	Hückel Approximation . . . . .	325
23.5	Simplified CI model for Polyenes . . . . .	327
23.6	Cyclic Polyene as a Model for Porphyrins . . . . .	328
23.7	The Four Orbital Model for Porphyrins . . . . .	329
23.8	Energy Transfer Processes . . . . .	331
	Problems . . . . .	332
<b>24</b>	<b>Incoherent Energy Transfer . . . . .</b>	<b>335</b>
24.1	Excited States . . . . .	335
24.2	Energy Transfer Mechanism . . . . .	337
24.3	Interaction Matrix Element . . . . .	338
24.4	Multipole Expansion of the Excitonic Interaction . . . . .	339
24.5	Energy Transfer Rate . . . . .	341
24.6	Spectral Overlap . . . . .	342
24.7	Energy Transfer in the Triplet State . . . . .	346
<b>25</b>	<b>Coherent Excitations in Photosynthetic Systems . . . . .</b>	<b>349</b>
25.1	Coherent Excitations . . . . .	350
25.1.1	Strongly Coupled Dimers . . . . .	350
25.1.2	Excitonic Structure of the Reaction Center . . . . .	355
25.1.3	Circular Molecular Aggregates . . . . .	356
25.1.4	Dimerized Systems of LHII . . . . .	362
25.2	Influence of Disorder . . . . .	367
25.2.1	Symmetry Breaking Local Perturbation . . . . .	367
25.2.2	Periodic Modulation . . . . .	369
25.2.3	Diagonal Disorder . . . . .	372
25.2.4	Off-Diagonal Disorder . . . . .	374
	Problems . . . . .	376

<b>26</b>	<b>Charge Transfer in DNA</b>	379
26.1	Diffusive Hole Transfer	380
26.2	Tunneling over Bridge States	382
26.3	Combined Transfer Mechanism	383
<b>27</b>	<b>Proton Transfer in Biomolecules</b>	385
27.1	The Proton Pump Bacteriorhodopsin	386
27.2	Born–Oppenheimer Separation	388
27.3	Nonadiabatic Proton Transfer (Small Coupling)	390
27.4	Strongly Bound Protons	391
27.5	Adiabatic Proton Transfer	393
<b>28</b>	<b>Proton Coupled Coherent Charge Transfer</b>	395
28.1	The Nonadiabatic Electronic Incoherent Step Transfer Model	395
28.1.1	The Rate Expression	396
28.1.2	Application of the Saddle Point Method	398
28.2	Heterogeneous Superexchange Coupling	402
28.3	Proton Coupled Superexchange	409
28.4	Coherent Dynamics	411
28.5	Coherent Oscillations	412

## Part VIII Molecular Motor Models

<b>29</b>	<b>Continuous Ratchet Models</b>	417
29.1	Transport Equations	418
29.2	A Simple Sawtooth Ratchet	423
29.3	Ratchets in the Low Temperature Limit	426
29.4	Chemical Transitions	429
29.5	The Two-State Model	435
29.5.1	The Chemical Cycle	436
29.5.2	The Fast Reaction Limit	441
29.5.3	The Fast Diffusion Limit	441
29.5.4	Operation Close to Thermal Equilibrium	443
29.6	Ratchet with Localized Reactions	445
	Problems	448
<b>30</b>	<b>Discrete Ratchet Models</b>	449
30.1	Linear Discrete Ratchets	449
30.2	Linear Model with Two Internal States	449

## Part IX Appendix

<b>Appendix A: The Grand Canonical Ensemble</b>	455
A.1 Grand Canonical Distribution	456
A.2 Connection to Thermodynamics	457

<b>Appendix B: Classical Approximation of Quantum Motion . . . . .</b>	<b>459</b>
<b>Appendix C: Time Correlation Function of the Displaced Harmonic</b>	
<b>Oscillator Model . . . . .</b>	<b>463</b>
C.1 Evaluation of the Time Correlation Function. . . . .	463
C.2 Boson Algebra. . . . .	465
C.2.1 Derivation of Theorem 1. . . . .	465
C.2.2 Derivation of Theorem 2. . . . .	466
C.2.3 Derivation of Theorem 3. . . . .	466
C.2.4 Derivation of Theorem 4. . . . .	467
<b>Appendix D: Complex Cotangent Function . . . . .</b>	<b>469</b>
<b>Appendix E: The Saddle Point Method. . . . .</b>	<b>471</b>
<b>Solutions . . . . .</b>	<b>475</b>
<b>References . . . . .</b>	<b>503</b>
<b>Index . . . . .</b>	<b>509</b>



Theoretical Molecular Biophysics

Scherer, P.O.J.; Fischer, S.F.

2017, XVI, 513 p. 226 illus., 27 illus. in color., Hardcover

ISBN: 978-3-662-55670-2