

Contents

Part I Statistical Mechanics of Biopolymers

1	Random Walk Models for the Conformation	3
1.1	The Freely Jointed Chain	3
1.1.1	Entropic Elasticity	4
1.1.2	Force–Extension Relation	6
1.2	Two-Component Model	9
1.2.1	Force–Extension Relation	9
1.2.2	Two-Component Model with Interactions	11
	Problems	16
2	Flory–Huggins Theory for Biopolymer Solutions	19
2.1	Monomeric Solution	19
2.2	Polymeric Solution	22
2.3	Phase Transitions	26
2.3.1	Stability Criterion	26
2.3.2	Critical Coupling	28
2.3.3	Phase Diagram	30
	Problems	33

Part II Protein Electrostatics and Solvation

3	Implicit Continuum Solvent Models	37
3.1	Potential of Mean Force	37
3.2	Dielectric Continuum Model	38
3.3	Born Model	39
3.4	Charges in a Protein	40
3.5	Generalized Born Models	43

4	Debye–Hückel Theory	45
4.1	Electrostatic Shielding by Mobile Charges	45
4.2	1–1 Electrolytes	46
4.3	Charged Sphere	47
4.4	Charged Cylinder	49
4.5	Charged Membrane (Gouy–Chapman Double Layer)	52
4.6	Stern Modification of the Double Layer	57
	Problems	58
5	Protonation Equilibria	61
5.1	Protonation Equilibria in Solution	61
5.2	Protonation Equilibria in Proteins	64
5.2.1	Apparent pK_a Values	65
5.2.2	Protonation Enthalpy	66
5.2.3	Protonation Enthalpy Relative to the Uncharged State	68
5.2.4	Statistical Mechanics of Protonation	69
5.3	Abnormal Titration Curves of Coupled Residues	70
	Problems	71

Part III Reaction Kinetics

6	Formal Kinetics	75
6.1	Elementary Chemical Reactions	75
6.2	Reaction Variable and Reaction Rate	75
6.3	Reaction Order	76
6.3.1	Zero-Order Reactions	77
6.3.2	First-Order Reactions	77
6.3.3	Second-Order Reactions	77
6.4	Dynamical Equilibrium	78
6.5	Competing Reactions	79
6.6	Consecutive Reactions	79
6.7	Enzymatic Catalysis	80
6.8	Reactions in Solutions	82
6.8.1	Diffusion-Controlled Limit	83
6.8.2	Reaction-Controlled Limit	84
	Problems	84
7	Kinetic Theory: Fokker–Planck Equation	87
7.1	Stochastic Differential Equation for Brownian Motion	87
7.2	Probability Distribution	89
7.3	Diffusion	90
7.3.1	Sharp Initial Distribution	91
7.3.2	Absorbing Boundary	92
7.4	Fokker–Planck Equation for Brownian Motion	93

7.5	Stationary Solution to the Focker–Planck Equation	94
7.6	Diffusion in an External Potential	96
7.7	Large Friction Limit: Smoluchowski Equation	98
7.8	Master Equation	98
	Problems	98
8	Kramers' Theory	101
8.1	Kramers' Model	101
8.2	Kramers' Calculation of the Reaction Rate	102
9	Dispersive Kinetics	107
9.1	Dichotomous Model	107
9.1.1	Fast Solvent Fluctuations	110
9.1.2	Slow Solvent Fluctuations	111
9.1.3	Numerical Example (Fig. 9.3)	112
9.2	Continuous Time Random Walk Processes	112
9.2.1	Formulation of the Model	112
9.2.2	Exponential Waiting Time Distribution	114
9.2.3	Coupled Equations	115
9.3	Power Time Law Kinetics	119
	Problems	121
 Part IV Transport Processes		
10	Nonequilibrium Thermodynamics	125
10.1	Continuity Equation for the Mass Density	125
10.2	Energy Conservation	127
10.3	Entropy Production	128
10.4	Phenomenological Relations	130
10.5	Stationary States	130
	Problems	132
11	Simple Transport Processes	133
11.1	Heat Transport	133
11.2	Diffusion in an External Electric Field	134
	Problems	136
12	Ion Transport Through a Membrane	139
12.1	Diffusive Transport	139
12.2	Goldman–Hodgkin–Katz Model	141
12.3	Hodgkin–Huxley Model	144

13	Reaction–Diffusion Systems	147
13.1	Derivation	147
13.2	Linearization	148
13.3	Fitzhugh–Nagumo Model	149

Part V Reaction Rate Theory

14	Equilibrium Reactions	155
14.1	Arrhenius Law	155
14.2	Statistical Interpretation of the Equilibrium Constant	157
15	Calculation of Reaction Rates	159
15.1	Collision Theory	159
15.2	Transition State Theory	162
15.3	Comparison Between Collision Theory and Transition State Theory	164
15.4	Thermodynamical Formulation of TST	165
15.5	Kinetic Isotope Effects	166
15.6	General Rate Expressions	168
15.6.1	The Flux Operator	168
	Problems	170
16	Marcus Theory of Electron Transfer	173
16.1	Phenomenological Description of ET	173
16.2	Simple Explanation of Marcus Theory	175
16.3	Free Energy Contribution of the Nonequilibrium Polarization	177
16.4	Activation Energy	180
16.5	Simple Model Systems	184
16.5.1	Charge Separation	186
16.5.2	Charge Shift	186
16.6	The Energy Gap as the Reaction Coordinate	187
16.7	Inner-Shell Reorganization	189
16.8	The Transmission Coefficient for Nonadiabatic Electron Transfer	189
	Problems	190

Part VI Elementary Photophysics

17	Molecular States	195
17.1	Born–Oppenheimer Separation	195
17.2	Nonadiabatic Interaction	197

18	Optical Transitions	201
18.1	Dipole Transitions in the Condon Approximation	201
18.2	Time Correlation Function Formalism	202
	Problems	203
19	The Displaced Harmonic Oscillator Model	205
19.1	The Time Correlation Function in the Displaced Harmonic Oscillator Approximation	205
19.2	High-Frequency Modes	206
19.3	The Short-Time Approximation	207
20	Spectral Diffusion	209
20.1	Dephasing	209
20.2	Gaussian Fluctuations	211
20.2.1	Long Correlation Time	212
20.2.2	Short Correlation Time	213
20.3	Markovian Modulation	214
	Problems	217
21	Crossing of Two Electronic States	219
21.1	Adiabatic and Diabatic States	219
21.2	Semiclassical Treatment	223
21.3	Application to Diabatic ET	224
21.4	Crossing in More Dimensions	225
	Problems	227
22	Dynamics of an Excited State	229
22.1	Green's Formalism	230
22.2	Ladder Model	233
22.3	A More General Ladder Model	237
22.4	Application to the Displaced Oscillator Model	240
	Problems	242

Part VII Elementary Photoinduced Processes

23	Photophysics of Chlorophylls and Carotenoids	247
23.1	MO Model for the Electronic States	248
23.2	The Free Electron Model for Polyenes	249
23.3	The LCAO Approximation	250
23.4	Hückel Approximation	251
23.5	Simplified CI Model for Polyenes	253
23.6	Cyclic Polyene as a Model for Porphyrins	253
23.7	The Four Orbital Model for Porphyrins	254
23.8	Energy Transfer Processes	256
	Problems	257

24 Incoherent Energy Transfer	259
24.1 Excited States	259
24.2 Interaction Matrix Element	260
24.3 Multipole Expansion of the Excitonic Interaction	262
24.4 Energy Transfer Rate	263
24.5 Spectral Overlap	264
24.6 Energy Transfer in the Triplet State	268
25 Coherent Excitations in Photosynthetic Systems	269
25.1 Coherent Excitations	270
25.1.1 Strongly Coupled Dimers	270
25.1.2 Excitonic Structure of the Reaction Center	273
25.1.3 Circular Molecular Aggregates	274
25.1.4 Dimerized Systems of LH2	280
25.2 Influence of Disorder	285
25.2.1 Symmetry-Breaking Local Perturbation	285
25.2.2 Periodic Modulation	287
25.2.3 Diagonal Disorder	290
25.2.4 Off-Diagonal Disorder	292
Problems	293
26 Ultrafast Electron Transfer Processes in the Photosynthetic Reaction Center	297
27 Proton Transfer in Biomolecules	301
27.1 The Proton Pump Bacteriorhodopsin	301
27.2 Born-Oppenheimer Separation	303
27.3 Nonadiabatic Proton Transfer (Small Coupling)	305
27.4 Strongly Bound Protons	306
27.5 Adiabatic Proton Transfer	308

Part VIII Molecular Motor Models

28 Continuous Ratchet Models	311
28.1 Transport Equations	311
28.2 Chemical Transitions	313
28.3 The Two-State Model	314
28.3.1 The Chemical Cycle	314
28.3.2 The Fast Reaction Limit	317
28.3.3 The Fast Diffusion Limit	317
28.4 Operation Close to Thermal Equilibrium	319
Problems	320
29 Discrete Ratchet Models	323
29.1 Linear Model with Two Internal States	324

Part IX Appendix

A	The Grand Canonical Ensemble	329
A.1	Grand Canonical Distribution	329
A.2	Connection to Thermodynamics	331
B	Time Correlation Function of the Displaced Harmonic Oscillator Model	333
B.1	Evaluation of the Time Correlation Function	333
B.2	Boson Algebra	334
B.2.1	Derivation of Theorem 1	334
B.2.2	Derivation of Theorem 2	335
B.2.3	Derivation of Theorem 3	335
B.2.4	Derivation of Theorem 4	336
C	The Saddle Point Method	339
	Solutions	341
	References	365
	Index	369