

CONTENTS

Preface	xv
1 Models of Polymer Chains	1
1.1 Introduction	1
1.1.1 Chain Architecture	1
1.1.2 Models of a Linear Polymer Chain	2
1.1.2.1 Models in a Continuous Space	2
1.1.2.2 Models in a Discrete Space	4
1.1.3 Real Chains and Ideal Chains	5
1.2 Ideal Chains	7
1.2.1 Random Walk in One Dimension	7
1.2.1.1 Random Walk	7
1.2.1.2 Mean Square Displacement	9
1.2.1.3 Step Motion	10
1.2.1.4 Normal Distribution	10
1.2.2 Random Walks in Two and Three Dimensions	12
1.2.2.1 Square Lattice	12
1.2.2.2 Lattice in Three Dimensions	13
1.2.2.3 Continuous Space	14
1.2.3 Dimensions of Random-Walk Chains	15
1.2.3.1 End-to-End Distance and Radius of Gyration	15
1.2.3.2 Dimensions of Ideal Chains	18
1.2.3.2 Dimensions of Chains with Short-Range Interactions	19
1.2.4 Problems	20
1.3 Gaussian Chain	23
1.3.1 What is a Gaussian Chain?	23
1.3.1.1 Gaussian Distribution	23
1.3.1.2 Contour Length	25
1.3.2 Dimension of a Gaussian Chain	25
1.3.2.1 Isotropic Dimension	25
1.3.2.2 Anisotropy	26

1.3.3 Entropy Elasticity	28
1.3.3.1 Boltzmann Factor	28
1.3.3.2 Elasticity	30
1.3.4 Problems	31
1.4 Real Chains	33
1.4.1 Excluded Volume	33
1.4.1.1 Excluded Volume of a Sphere	33
1.4.1.2 Excluded Volume in a Chain Molecule	34
1.4.2 Dimension of a Real Chain	36
1.4.2.1 Flory Exponent	36
1.4.2.2 Experimental Results	37
1.4.3 Self-Avoiding Walk	39
1.4.4 Problems	40
1.5 Semirigid Chains	41
1.5.1 Examples of Semirigid Chains	41
1.5.2 Wormlike Chain	43
1.5.2.1 Model	43
1.5.2.2 End-to-End Distance	44
1.5.2.3 Radius of Gyration	45
1.5.2.4 Estimation of Persistence Length	46
1.5.3 Problems	47
1.6 Branched Chains	49
1.6.1 Architecture of Branched Chains	49
1.6.2 Dimension of Branched Chains	50
1.6.3 Problems	52
1.7 Molecular Weight Distribution	55
1.7.1 Average Molecular Weights	55
1.7.1.1 Definitions of the Average Molecular Weights	55
1.7.1.2 Estimation of the Averages and the Distribution	57
1.7.2 Typical Distributions	58
1.7.2.1 Poisson Distribution	58
1.7.2.2 Exponential Distribution	59
1.7.2.3 Log-Normal Distribution	60
1.7.3 Problems	62
1.8 Concentration Regimes	63
1.8.1 Concentration Regimes for Linear Flexible Polymers	63
1.8.2 Concentration Regimes for Rodlike Molecules	65
1.8.3 Problems	66

2 Thermodynamics of Dilute Polymer Solutions	69
2.1 Polymer Solutions and Thermodynamics	69
2.2 Flory-Huggins Mean-Field Theory	70
2.2.1 Model	70
2.2.1.1 Lattice Chain Model	70
2.2.1.2 Entropy of Mixing	72
2.2.1.3 χ Parameter	72
2.2.1.4 Interaction Change Upon Mixing	74
2.2.2 Free Energy, Chemical Potentials, and Osmotic Pressure	75
2.2.2.1 General Formulas	75
2.2.2.2 Chemical Potential of a Polymer Chain in Solution	77
2.2.3 Dilute Solutions	77
2.2.3.1 Mean-Field Theory	77
2.2.3.2 Virial Expansion	78
2.2.4 Coexistence Curve and Stability	80
2.2.4.1 Replacement Chemical Potential	80
2.2.4.2 Critical Point and Spinodal Line	81
2.2.4.3 Phase Separation	82
2.2.4.4 Phase Diagram	84
2.2.5 Polydisperse Polymer	87
2.2.6 Problems	89
2.3 Phase Diagram and Theta Solutions	99
2.3.1 Phase Diagram	99
2.3.1.1 Upper and Lower Critical Solution Temperatures	99
2.3.1.2 Experimental Methods	100
2.3.2 Theta Solutions	101
2.3.2.1 Theta Temperature	101
2.3.2.2 Properties of Theta Solutions	103
2.3.3 Coil-Globule Transition	105
2.3.4 Solubility Parameter	107
2.3.5 Problems	108
2.4 Static Light Scattering	108
2.4.1 Sample Geometry in Light-Scattering Measurements	108
2.4.2 Scattering by a Small Particle	110
2.4.3 Scattering by a Polymer Chain	112
2.4.4 Scattering by Many Polymer Chains	115
2.4.5 Correlation Function and Structure Factor	117
2.4.5.1 Correlation Function	117
2.4.5.2 Relationship Between the Correlation Function and Structure Factor	117

2.4.5.3	Examples in One Dimension	119
2.4.6	Structure Factor of a Polymer Chain	120
2.4.6.1	Low-Angle Scattering	120
2.4.6.2	Scattering by a Gaussian Chain	121
2.4.6.3	Scattering by a Real Chain	124
2.4.6.4	Form Factors	125
2.4.7	Light Scattering of a Polymer Solution	128
2.4.7.1	Scattering in a Solvent	128
2.4.7.2	Scattering by a Polymer Solution	129
2.4.7.3	Concentration Fluctuations	131
2.4.7.4	Light-Scattering Experiments	132
2.4.7.5	Zimm Plot	133
2.4.7.6	Measurement of dn/dc	135
2.4.8	Other Scattering Techniques	136
2.4.8.1	Small-Angle Neutron Scattering (SANS)	136
2.4.8.2	Small-Angle X-Ray Scattering (SAXS)	139
2.4.9	Problems	139
2.5	Size Exclusion Chromatography and Confinement	148
2.5.1	Separation System	148
2.5.2	Plate Theory	150
2.5.3	Partitioning of Polymer with a Pore	151
2.5.3.1	Partition Coefficient	151
2.5.3.2	Confinement of a Gaussian Chain	153
2.5.3.3	Confinement of a Real Chain	156
2.5.4	Calibration of SEC	158
2.5.5	SEC With an On-Line Light-Scattering Detector	160
2.5.6	Problems	162
APPENDIXES		
2.A:	Review of Thermodynamics for Colligative Properties in Nonideal Solutions	164
2.A.1	Osmotic Pressure	164
2.A.2	Vapor Pressure Osmometry	164
2.B:	Another Approach to Thermodynamics of Polymer Solutions	165
2.C:	Correlation Function of a Gaussian Chain	166
3	Dynamics of Dilute Polymer Solutions	167
3.1	Dynamics of Polymer Solutions	167
3.2	Dynamic Light Scattering and Diffusion of Polymers	168
3.2.1	Measurement System and Autocorrelation Function	168
3.2.1.1	Measurement System	168
3.2.1.2	Autocorrelation Function	169
3.2.1.3	Photon Counting	170

3.2.2	Autocorrelation Function	170
3.2.2.1	Baseline Subtraction and Normalization	170
3.2.2.2	Electric-Field Autocorrelation Function	172
3.2.3	Dynamic Structure Factor of Suspended Particles	172
3.2.3.1	Autocorrelation of Scattered Field	172
3.2.3.2	Dynamic Structure Factor	174
3.2.3.3	Transition Probability	174
3.2.4	Diffusion of Particles	176
3.2.4.1	Brownian Motion	176
3.2.4.2	Diffusion Coefficient	177
3.2.4.3	Gaussian Transition Probability	178
3.2.4.4	Diffusion Equation	179
3.2.4.5	Concentration	179
3.2.4.6	Long-Time Diffusion Coefficient	180
3.2.5	Diffusion and DLS	180
3.2.5.1	Dynamic Structure Factor and Mean Square Displacement	180
3.2.5.2	Dynamic Structure Factor of a Diffusing Particle	181
3.2.6	Dynamic Structure Factor of a Polymer Solution	182
3.2.6.1	Dynamic Structure Factor	182
3.2.6.2	Long-Time Behavior	183
3.2.7	Hydrodynamic Radius	184
3.2.7.1	Stokes-Einstein Equation	184
3.2.7.2	Hydrodynamic Radius of a Polymer Chain	185
3.2.8	Particle Sizing	188
3.2.8.1	Distribution of Particle Size	188
3.2.8.2	Inverse-Laplace Transform	188
3.2.8.3	Cumulant Expansion	189
3.2.8.4	Example	190
3.2.9	Diffusion From Equation of Motion	191
3.2.10	Diffusion as Kinetics	193
3.2.10.1	Fick's Law	193
3.2.10.2	Diffusion Equation	195
3.2.10.3	Chemical Potential Gradient	196
3.2.11	Concentration Effect on Diffusion	196
3.2.11.1	Self-Diffusion and Mutual Diffusion	196
3.2.11.2	Measurement of Self-Diffusion Coefficient	
3.2.11.3	Concentration Dependence of the Diffusion Coefficients	198
3.2.12	Diffusion in a Nonuniform System	200
3.2.13	Problems	201
3.3	Viscosity	209
3.3.1	Viscosity of Solutions	209

3.3.1.1	Viscosity of a Fluid	209
3.3.1.2	Viscosity of a Solution	211
3.3.2	Measurement of Viscosity	213
3.3.3	Intrinsic Viscosity	215
3.3.4	Flow Field	217
3.3.5	Problems	219
3.4	Normal Modes	221
3.4.1	Rouse Model	221
3.4.1.1	Model for Chain Dynamics	221
3.4.1.2	Equation of Motion	222
3.4.2	Normal Coordinates	223
3.4.2.1	Definition	223
3.4.2.2	Inverse Transformation	226
3.4.3	Equation of Motion for the Normal Coordinates in the Rouse Model	226
3.4.3.1	Equation of Motion	226
3.4.3.2	Correlation of Random Force	228
3.4.3.3	Formal Solution	229
3.4.4	Results of the Normal-Coordinates	229
3.4.4.1	Correlation of $\mathbf{q}_i(t)$	229
3.4.4.2	End-to-End Vector	230
3.4.4.3	Center-of-Mass Motion	231
3.4.4.4	Evolution of $\mathbf{q}_i(t)$	231
3.4.5	Results for the Rouse Model	232
3.4.5.1	Correlation of the Normal Modes	232
3.4.5.2	Correlation of the End-to-End Vector	234
3.4.5.3	Diffusion Coefficient	234
3.4.5.4	Molecular Weight Dependence	234
3.4.6	Zimm Model	234
3.4.6.1	Hydrodynamic Interactions	234
3.4.6.2	Zimm Model in the Theta Solvent	236
3.4.6.3	Hydrodynamic Radius	238
3.4.6.4	Zimm Model in the Good Solvent	238
3.4.7	Intrinsic Viscosity	239
3.4.7.1	Extra Stress by Polymers	239
3.4.7.2	Intrinsic Viscosity of Polymers	241
3.4.7.3	Universal Calibration Curve in SEC	243
3.4.8	Dynamic Structure Factor	243
3.4.8.1	General Formula	243
3.4.8.2	Initial Slope in the Rouse Model	247
3.4.8.3	Initial Slope in the Zimm Model, Theta Solvent	247
3.4.8.4	Initial Slope in the Zimm Model, Good Solvent	248
3.4.8.5	Initial Slope: Experiments	249
3.4.9	Motion of Monomers	250

3.4.9.1	General Formula	250
3.4.9.2	Mean Square Displacement: Short-Time Behavior Between a Pair of Monomers	251
3.4.9.3	Mean Square Displacement of Monomers	252
3.4.10	Problems	257
3.5	Dynamics of Rodlike Molecules	262
3.5.1	Diffusion Coefficients	262
3.5.2	Rotational Diffusion	263
3.5.2.1	Pure Rotational Diffusion	263
3.5.2.2	Translation-Rotational Diffusion	266
3.5.3	Dynamic Structure Factor	266
3.5.4	Intrinsic Viscosity	269
3.5.5	Dynamics of Wormlike Chains	269
3.5.6	Problems	270
APPENDICES		
3.A:	Evaluation of $\langle \mathbf{q}_i^2 \rangle_{\text{eq}}$	271
3.B:	Evaluation of $\langle \exp[i\mathbf{k} \cdot (A\mathbf{q} - B\mathbf{p})] \rangle$	273
3.C:	Initial Slope of $S_1(\mathbf{k}, t)$	274
4	Thermodynamics and Dynamics of Semidilute Solutions	277
4.1	Semidilute Polymer Solutions	277
4.2	Thermodynamics of Semidilute Polymer Solutions	278
4.2.1	Blob Model	278
4.2.1.1	Blobs in Semidilute Solutions	278
4.2.1.2	Size of the Blob	279
4.2.1.3	Osmotic Pressure	282
4.2.1.4	Chemical Potential	285
4.2.2	Scaling Theory and Semidilute Solutions	286
4.2.2.1	Scaling Theory	286
4.2.2.2	Osmotic Compressibility	289
4.2.2.3	Correlation Length and Monomer Density Correlation Function	289
4.2.2.4	Chemical Potential	294
4.2.2.5	Chain Contraction	295
4.2.2.6	Theta Condition	296
4.2.3	Partitioning with a Pore	298
4.2.3.1	General Formula	298
4.2.3.2	Partitioning at Low Concentrations	299
4.2.3.3	Partitioning at High Concentrations	300
4.2.4	Problems	301

4.3 Dynamics of Semidilute Solutions	307
4.3.1 Cooperative Diffusion	307
4.3.2 Tube Model and Reptation Theory	310
4.3.2.1 Tube and Primitive Chain	310
4.3.2.2 Tube Renewal	312
4.3.2.3 Disengagement	313
4.3.2.4 Center-of-Mass Motion of the Primitive Chain	315
4.3.2.5 Estimation of the Tube Diameter	318
4.3.2.6 Measurement of the Center-of-Mass Diffusion Coefficient	319
4.3.2.7 Constraint Release	320
4.3.2.8 Diffusion of Polymer Chains in a Fixed Network	321
4.3.2.9 Motion of the Monomers	322
4.3.3 Problems	324
References	325
Further Readings	326
Appendices	328
A1 Delta Function	328
A2 Fourier Transform	329
A3 Integrals	331
A4 Series	332
Index	333