

# Contents

<b>1</b>	<b>Introduction</b>	1
1.1	Complex Fluids and Polymers	2
1.1.1	Complex Systems	2
1.1.2	Complex Fluids	3
1.1.3	Mesoscopic Structures in Complex Fluids	7
1.2	Polymers: A Typical Example of Complex Fluids	8
1.2.1	Molecular Structure of Polymers	8
1.2.2	Mesoscopic and Macroscopic Properties of Polymers	10
1.3	Modeling the Physical Phenomena of Polymers	11
1.3.1	Modeling Mesoscopic Structures	11
1.3.2	Static Properties	12
1.3.3	Dynamic Properties	14
1.3.4	Physical Properties and Gaussian Chain Statistics	14
<b>2</b>	<b>Gaussian Chain Model and Statistics of Polymers</b>	17
2.1	A Simple Model of a Polymer Chain: The Lattice Model	17
2.1.1	Definition of the Lattice Model of Polymers	17
2.1.2	Ideal Chain Statistics of Lattice Models	25
2.2	Bead-Spring Model of Polymer Chain and Gaussian Chain Statistics	34
2.2.1	Coarse-Graining Procedure and Bead-Spring Model	34
2.3	Statistical Mechanical Theory of Equilibrium Conformations of a Gaussian Chain	37
2.3.1	Ideal Chain Statistics	37
2.3.2	Correlation Functions and Scattering Functions of an Ideal Chain	43
2.3.3	Statistical Mechanics of Chains with Interactions and Approximate Theories	48
2.3.4	Statistical Properties of Many-Chain Systems	54
2.4	Dynamical Models of a Polymer Chain Based on a Molecular Description	62
2.4.1	Formulation of Brownian Motion	62
2.4.2	Rouse Model of a Single Polymer Chain in a Solvent	66
2.4.3	Hydrodynamic Effects in Dilute Polymer Solutions	73

X      Contents

2.5	Justification of the Gaussian Chain Model from a Microscopic Point of View . . . . .	80
2.5.1	Full Atomistic Model of Polymer Chains . . . . .	80
2.5.2	United Atom Model . . . . .	81
2.6	Statistical Theories and Experiments on Semi-Flexible Chains . . . . .	84
2.6.1	Worm-Like Chain Model . . . . .	84
2.6.2	Statistical Properties of a Stretched Worm-Like Chain	86
2.6.3	Experiments on Worm-Like Chains Using Biopolymers	90
2.7	Molecular Simulations of Polymer Dynamics . . . . .	95
2.7.1	Molecular Simulation Methods . . . . .	95
2.7.2	Models of Interaction Potentials for Coarse-Grained Chains . . . . .	96
2.7.3	Examples of Molecular Simulations . . . . .	96
	Exercises . . . . .	99
<b>3</b>	<b>Mesoscopic Structures and Self-Consistent Field Theory</b> . . . . .	<b>101</b>
3.1	Mesoscopic Phenomena in Polymer Systems . . . . .	101
3.2	Formulation and Simple Examples of the Self-Consistent Field Theory of Polymers . . . . .	103
3.2.1	Mean Field Approximation and Self-Consistent Field . . . . .	105
3.2.2	Path Integral Formalism for Polymers . . . . .	106
3.2.3	Classical Approximation for Self-Consistent Field Theory . . . . .	111
3.3	Numerical Methods for the Self-Consistent Field Theory of Polymers . . . . .	121
3.3.1	Functionals, Functional Derivatives and Functional Integrals . . . . .	122
3.3.2	General Expression for the Free Energy . . . . .	126
3.3.3	Numerical Solutions of Self-Consistent Field Equations . . . . .	134
3.3.4	Examples of Numerical Simulations Using Self-Consistent Field Theory . . . . .	142
	Exercises . . . . .	151
<b>4</b>	<b>Ginzburg–Landau Theory</b> . . . . .	<b>153</b>
4.1	Formulation of the Ginzburg–Landau Theory . . . . .	153
4.1.1	Ginzburg–Landau Model . . . . .	153
4.1.2	Expansion of the Free Energy . . . . .	159
4.1.3	Evaluation of Expansion Coefficients Using the Random Phase Approximation . . . . .	162
4.2	Applications of the Ginzburg–Landau Theory . . . . .	172
4.2.1	Phase Diagram of Block Copolymer Melts . . . . .	172
4.2.2	Extensions to Dynamical Processes . . . . .	174
	Exercises . . . . .	177

<b>5 Macroscopic Viscoelastic Theory of Polymers</b> .....	179
5.1 Viscoelastic Properties of Polymeric Liquids .....	179
5.1.1 Polymers and Viscoelasticity .....	179
5.1.2 Hydrodynamic Descriptions of Viscoelasticity .....	186
5.2 Reptation Theory for Linear Polymers .....	190
5.2.1 Concept of Reptation Theory .....	190
5.2.2 Stress Relaxation Function .....	192
5.3 Extensions of Reptation Theory and Nonlinear Viscoelasticity	201
5.3.1 Contour Length Fluctuations .....	203
5.3.2 Chain Retraction .....	205
5.3.3 Constraint Release .....	206
5.3.4 Contribution to Viscoelasticity from Phase-Separated Domains .....	208
Exercises .....	210
<b>References</b> .....	211
<b>Index</b> .....	213