CONTENTS

Preface xviii

Acknowledgments xxi

PART I FUNDAMENTALS 1

Chapter 1 Introduction to Complex Fluids 3

1.1 Complex Fluids Versus Classical Solids and Liquids 3

1.2 Examples of Complex Fluids 4

1.2.1 Foods 4

1.2.2 Biofluids 7

1.2.3 Personal Care Products 8

1.2.4 Electronic and Optical Materials 8

1.2.5 Polymers 9

1.2.6 Other Examples 10

1.3 Rheological Measurements and Properties 10

1.3.1 Shearing Flow 10

1.3.1.1 Flow Geometries 10

1.3.1.2 Steady-State Shear Viscosity 12

1.3.1.3 Transient Shear Viscosity 12

1.3.1.4 Storage and Loss Moduli 13

1.3.1.5 Types of Rheological Response 14

1.3.1.6 Deborah Number, Weissenberg Number, and Peclet Number 18

1.3.2 Extensional Flow 18

1.3.3 Mixed Flow 20

1.4 Kinematics and Stress 21

1.4.1 The Velocity Gradient Tensor 22

1.4.1.1 Shearing Flow 23

1.4.1.2 Extensional Flow 23

1.4.1.3 Mixed Flow 24

1.4.2 The Deformation Gradient and Finger Tensors 24

1.4.2.1 The Deformation Gradient Tensor **24**
1.4.2.2 The Finger Tensor **25**
1.4.3 The Stress Tensor **27**
1.5 Flow, Slip, and Yield **30**
1.5.1 Flow **30**
1.5.2 Wall Slip **31**
1.5.2.1 Methods of Measuring Slip **32**
1.5.2.1.1 Gap-Dependent Apparent Shear Rate **32**
1.5.2.1.2 Effect of Surface Treatment **32**
1.5.2.1.3 Particle Tracers **32**
1.5.2.1.4 Evanescent Waves **33**
1.5.2.1.5 Laser-Doppler Velocimetry **33**
1.5.2.1.6 Rheo-NMR **33**
1.5.2.2 The Extrapolation Length **33**
1.5.2.3 Estimate of Extrapolation Length for Simple Liquids **34**
1.5.3 Yield **35**
1.6 Structural Probes of Complex Fluids **38**
1.6.1 Microscopy **38**
1.6.2 Light, X-Ray, and Neutron Scattering **39**
1.6.2.1 Photon Correlation Spectroscopy **41**
1.6.2.2 Diffusing-Wave Spectroscopy **42**
1.6.3 Polarimetry **42**
1.6.4 Linear Dichroism **43**
1.6.5 Polarized Light Scattering **43**
1.6.6 Raman Scattering and Fluorescence Polarization **43**
1.6.7 Other Methods **44**
1.7 Computational Methods **46**
1.7.1 Molecular Dynamics Simulations **46**
1.7.2 Brownian Dynamics Simulations **47**
1.7.3 Monte Carlo Sampling **47**
1.7.4 Numerical Solution of Composition-Field Equations **48**
1.7.5 Suspension Simulations **49**
1.7.6 Boundary Conditions **49**
1.8 The Stress Tensor **49**
1.9 Summary **50**
References **50**
Problems and Worked Examples **55**

Chapter 2 Basic Forces 61
2.1 Introduction **61**
2.2 Excluded-Volume Interactions **61**
2.2.1 Hard Spheres **62**

2.2.2 Rigid Nonspherical Particles or Molecules: The Nematic Phase **64**
2.2.2.1 Onsager Theory **65**
2.2.2.2 Maier–Saupe Theory **67**
2.2.2.3 Flory Lattice Theory **68**
2.2.3 Flexible Macromolecules **69**
2.2.3.1 Polydispersity **69**
2.2.3.2 Random-Walk Statistics: The Freely Jointed Chain **71**
2.2.3.3 Long-Range Excluded-Volume Effects in Solutions **73**
2.2.3.4 Local Packing Effects in Melts **74**
2.2.4 Semiflexible Macromolecules **75**
2.3 Van Der Waals Interactions **78**
2.3.1 Molecular Mixtures **78**
2.3.1.1 Dipolar Interactions: London, Keesom, and Debye Forces **78**
2.3.1.2 The Flory–Huggins Model **80**
2.3.1.3 Theories for the χ Parameter **84**
2.3.2 Suspensions **85**
2.4 Electrostatic Interactions **87**
2.4.1 The Poisson–Boltzmann Equation **88**
2.4.2 A Charged Surface and Its Double Layer **88**
2.4.3 The Force Between Two Charged Plates **91**
2.4.4 Interaction Potentials for Spheres **92**
2.5 Hydrogen-Bonding, Hydrophobic, and Other Interactions **95**
2.6 Summary **96**
References **97**
Problems and Worked Examples **99**

PART II POLYMERS, GLASSY LIQUIDS, AND POLYMER GELS 105

Chapter 3 Polymers 107
3.1 Introduction **107**
3.2 Equilibrium Properties **112**
3.3 Intrinsic Viscosity and Overlap Concentration **113**
3.4 Elementary Molecular Theories **114**
3.4.1 The Polymer Stress and Birefringence Tensors **114**
3.4.2 Rubber Elasticity Theory **116**
3.4.3 The Temporary Network Model **119**
3.4.4 The Elastic Dumbbell Model **123**

3.4.5 The Rouse Model **126**

3.5 Linear Viscoelasticity and Time–Temperature Superposition **128**
3.5.1 Distribution of Relaxation Times **128**
3.5.2 Time–Temperature Superposition **129**

3.6 The Rheology of Dilute Polymer Solutions **132**
3.6.1 Linear Rheology **132**
3.6.1.1 Molecular-Weight Scaling Laws **132**
3.6.1.2 Complex Modulus: The Zimm Theory **134**
3.6.1.3 High-Frequency Behavior **136**
3.6.2 Nonlinear Rheology **136**
3.6.2.1 Experiments **137**
3.6.2.1.1 Shearing Flow **138**
3.6.2.1.2 Extensional Flow **140**
3.6.2.1.3 Mixed Flow **141**
3.6.2.2 Simple Theories **142**
3.6.2.2.1 Finite Extensibility **142**
3.6.2.2.2 Conformation-Dependent Drag Coefficient **145**

3.7 The Rheology of Entangled Polymers **149**
3.7.1 Reptation **151**
3.7.2 Nonreptative Relaxation Mechanisms **152**
3.7.2.1 Primitive-Path Fluctuations **154**
3.7.2.2 Constraint Release **155**
3.7.3 Evidence for Reptation **156**
3.7.4 The Doi–Edwards Constitutive Equation **156**
3.7.4.1 Linear Relaxation Modulus **157**
3.7.4.2 Nonlinear Modulus and Damping Function **158**
3.7.4.3 Stress Tensor After a Step Strain **160**
3.7.4.4 Constitutive Equation **161**
3.7.5 Predictions of Reptation Theories **162**
3.7.5.1 Steady-State Shear and Extension **162**
3.7.5.2 Stress Overshoots **165**
3.7.5.3 Anomalous Rheology **166**
3.7.6 Effects of Polydispersity and Branching **168**
3.7.6.1 Polydisperse Melts **168**
3.7.6.2 Star Molecules **169**
3.7.6.3 Melts with Irregular Long-Chain Branching **170**
3.7.6.4 Semiempirical Constitutive Equations **171**

3.8 Summary **174**
References **175**
Problems and Worked Examples **180**

Chapter 4 Glassy Liquids 189
4.1 Introduction **189**
4.2 Phenomenology of the Glass Transition **191**
4.3 Free-Volume Theories **196**
4.4 Entropy Theories **198**
4.4.1 Gibbs–DiMarzio Theory **200**
4.4.2 Adam–Gibbs Theory **201**
4.4.3 Miller's Theory **203**
4.5 Nonlinear Relaxation and Aging **206**
4.6 Mode-Coupling Theory and Colloidal Hard-Sphere Glasses **212**
4.7 Simulations of Analog Models **219**
4.7.1 Square Tiling Model **219**
4.7.2 Facilitated Ising Model **220**
4.7.3 Bond Fluctuation Model **223**
4.8 Rheology of Glassy Liquids **223**
4.8.1 Linear Rheology **223**
4.8.2 Nonlinear Rheology **225**
4.8.3 Thermorheological Behavior **225**
4.9 Summary **228**
References **229**

Chapter 5 Polymer Gels 232
5.1 Introduction **232**
5.2 Gelation Theories **235**
5.2.1 Percolation Theory **235**
5.2.2 Flory–Stockmayer Theory **236**
5.2.3 Fractals and Self-Similarity **237**
5.3 Rheology of Chemical Gels and Near-Gels **238**
5.4 Rheology of Physical Gels **243**
5.4.1 Telechelic Polymers **248**
5.4.2 Entangled "Sticky" Chains **254**
5.5 Summary **258**
References **258**

PART III SUSPENSIONS 261

Chapter 6 Particulate Suspensions 263
6.1 Introduction **263**
6.2 Hard, and Slightly Deformable, Spheres **264**
6.2.1 Zero-Shear Viscosity **265**

6.2.2 Shear Thinning **267**
6.2.3 Shear Thickening **273**
6.2.4 Suspension Modulus **274**
6.2.5 Normal Stress Differences **278**
6.2.6 Other Nonlinear Properties **279**
6.3 Nonspherical Particles **279**
6.3.1 Dilute Suspensions **279**
6.3.1.1 Jeffery Orbits **279**
6.3.1.2 Rotary Diffusivities **280**
6.3.1.3 Stresses for Suspensions of Spheroids **282**
6.3.1.4 Stresses for Suspensions of High-Aspect Ratio Particles and Molecules **284**
6.3.2 Semidilute Solutions and Suspensions of Rods **285**
6.3.2.1 Brownian Rods **285**
6.3.2.2 Non-Brownian Fiber Suspensions **291**
6.4 Electrically Charged Particles **297**
6.4.1 Viscosity **299**
6.4.2 Yield Stress and Modulus **301**
6.4.3 Flow Mechanisms **303**
6.4.4 Shear Thickening and Normal Stress Differences **304**
6.5 Particles in Viscoelastic Liquids: "Filled Melts" **309**
6.5.1 Spherical Particles **309**
6.5.2 Rod-like Particles **312**
6.6 Summary **313**
References **314**
Problems and Worked Examples **318**

Chapter 7 Particulate Gels 324
7.1 Introduction **324**
7.2 Particle Interactions in Suspensions **325**
7.2.1 Interparticle Potentials **325**
7.2.2 Electrostatic Stabilization **329**
7.2.3 Flocculation and Gelation **330**
7.2.4 Thermoreversible Gelation **332**
7.2.5 Gelation and Phase Separation **334**
7.3 Rheology of Particulate Gels **337**
7.3.1 The Rheology of Weakly Flocculated Gels **338**
7.3.2 The Rheology of Strongly Flocculated Gels **342**
7.3.3 Theory **350**
7.3.3.1 Yield Stress and Elastic Modulus **350**
7.3.3.2 Shear Viscosity at High Shear Rates **353**
7.4 Summary **355**
References **355**
Problems and Worked Examples **357**

Chapter 8 Electro- and Magnetoresponsive Suspensions 360
8.1 Introduction **360**
8.2 Electrorheological Fluids **360**
8.2.1 The Simple Polarization Model **363**
8.2.1.1 Electrostatic Forces **363**
8.2.1.2 Hydrodynamic Forces **365**
8.2.1.3 Steric Forces **365**
8.2.1.4 Brownian Forces **365**
8.2.1.5 The Particle Evolution Equation **366**
8.2.1.6 The Stress Tensor **367**
8.2.2 Electrorheological Phenomena **367**
8.2.2.1 Aggregation Kinetics **367**
8.2.2.2 Static Yield Stress **368**
8.2.2.3 Steady Shearing Flow **370**
8.2.2.4 Oscillatory Electric Field **372**
8.2.2.5 Dynamic Moduli **374**
8.2.3 Other Electrorheological Effects **375**
8.3 Magnetorheological Fluids **376**
8.4 Ferrofluids **378**
8.4.1 Magnetic Dipole–Dipole Interactions **379**
8.4.2 Dipole Orientations in an Applied Magnetic Field **380**
8.4.3 Viscosity of a Ferrofluid **382**
8.4.4 Ferrofluid Phenomena **383**
8.5 Summary **385**
References **385**

Chapter 9 Foams, Emulsions, and Blends 388
9.1 Introduction **388**
9.2 Emulsion Preparation **388**
9.2.1 Phase Separation **389**
9.2.1.1 Early Stage **392**
9.2.1.2 Intermediate Stage **394**
9.2.1.3 Late Stage **394**
9.2.2 Mechanical Mixing and Droplet Dynamics **398**
9.2.2.1 Droplet Breakup in Emulsions **399**
9.2.2.2 Droplet Coalescence in Emulsions **402**
9.2.2.3 Droplet Dynamics in Immiscible Polymer Blends **403**
9.3 Rheology of Emulsions and Immiscible Blends **409**
9.3.1 Steady Shear Viscosity and Normal Stresses **410**
9.3.2 Linear Viscoelasticity **413**
9.3.3 Nonlinear Transient Viscoelasticity: The Doi–Ohta Theory **416**
9.3.4 Rheology at High Droplet Volume Fraction **420**

9.3.4.1 Large Droplets **421**
9.3.4.2 Small Droplets **421**
9.3.4.3 Droplets of Intermediate Size **422**
9.4 Structure and Coarsening of Foams **425**
9.4.1 Structure of Dry Foams **426**
9.4.2 Coarsening **428**
9.4.2.1 Coarsening Theory for Two-Dimensional Foams **429**
9.4.2.2 Coarsening Theory for Three-Dimensional Foams **431**
9.5 Rheology of Foams **431**
9.5.1 Cellular Foam Models **431**
9.5.2 Other Models **435**
9.6 Summary **436**
References **437**

PART IV LIQUID CRYSTALS AND SELF-ASSEMBLING FLUIDS 441

Chapter 10 Liquid Crystals 443
10.1 Introduction **443**
10.2 Nematics **446**
10.2.1 Ericksen's Transversely Isotropic Fluid **448**
10.2.2 Frank–Oseen Theory **451**
10.2.3 Leslie–Ericksen Theory **452**
10.2.4 Theory for the Leslie Viscosities and Frank Constants **455**
10.2.4.1 The Leslie Viscosities **455**
10.2.4.2 The Frank Constants **459**
10.2.4.3 Discotic Nematics **460**
10.2.5 Shearing of Flow-Aligning Nematics **461**
10.2.6 Shearing of Tumbling Nematics **463**
10.2.6.1 Sudden Start-up of Shearing **463**
10.2.6.2 Gradual Increase in Shear Rate **467**
10.2.7 Disclination Dynamics **470**
10.3 Cholesterics: Chiral Nematics **476**
10.4 Smectics **478**
10.4.1 Types of Smectics **478**
10.4.2 Smectic Viscosities **480**
10.4.3 Smectic Elasticities **481**
10.4.4 Smectic Defects **482**
10.4.4.1 Focal Conics **482**
10.4.4.2 Other Defects **485**
10.4.5 Shearing Flow of Aligned Smectics **486**
10.4.5.1 Parallel, or "c," Orientation **486**

10.4.5.2 Transverse, or "b," Orientation **487**
10.4.5.3 Perpendicular, or "a," Orientation **487**
10.4.6 Steady Shearing Flow of Defect-Ridden Smectics **487**
10.4.7 Dynamic Modulus **488**
10.4.8 Shear Alignment **490**
10.5 Summary **491**
References **492**
Problems and Worked Examples **495**

Chapter 11 Liquid-Crystalline Polymers **503**
11.1 Introduction **503**
11.2 Molecular Characteristics of Liquid-Crystalline Polymers **504**
11.3 Flow Properties of Nematic LCPs **507**
11.3.1 Dependence of Viscosity on Concentration or Temperature **507**
11.3.2 Region I Shear Thinning **509**
11.3.3 Negative First Normal Stress Differences **511**
11.3.4 Transient Shear Stresses **514**
11.3.5 Textures of Sheared LCPs **515**
11.3.6 The Role of Microcrystallites and Chemical Reactions **518**
11.4 Molecular Dynamics of Polymeric Nematics **519**
11.4.1 Molecular and Gradient Elasticities **519**
11.4.2 The Smoluchowski Equation **520**
11.4.3 Doi's Approximate Solution of the Smoluchowski Equation **522**
11.4.4 Tumbling and Flow-Aligning **523**
11.5 Molecular Theory for the Rheology of Polymeric Nematics **526**
11.5.1 Leslie Viscosities and Frank Constants of Monodomains **526**
11.5.2 Rheology in Region III: The Effect of Molecular Elasticity **532**
11.5.3 Rheology in Region II: The Effect of Texture Elasticity **537**
11.5.4 Rheology in Region I **544**
11.6 Summary **546**
References **547**

Chapter 12 Surfactant Solutions **551**
12.1 Introduction **551**
12.2 Methods of Predicting Microstructures **553**

12.2.1 Packing Argument **553**
12.2.2 Surface-Curvature Argument **554**
12.2.3 Molecular Simulations **554**
12.3 Disordered Micellar Solutions **555**
12.3.1 Micellar Shapes and Shape Transitions **556**
12.3.1.1 Spherical Micelles **557**
12.3.1.2 Micellar Growth and Transition to Cylindrical Shapes **558**
12.3.1.3 Cylindrical Micelles **560**
12.3.2 Rheology of Disordered Solutions of Spherical Micelles **562**
12.3.3 Rheology of Dilute Wormy Micellar Solutions **562**
12.3.4 Rheology of Entangled Wormy Micellar Solutions **564**
12.3.4.1 Cates' Reptation Model **568**
12.3.4.2 The Effect of Added Salts **570**
12.3.4.3 The Effect of Temperature **573**
12.3.4.4 Nonlinear Rheology **574**
12.4 Surfactant Liquid Crystals **576**
12.4.1 Phase Behavior **576**
12.4.1.1 Nematic, Hexagonal, and Lamellar Phases **576**
12.4.1.2 Strut, Mesh, and Ribbon Phases **579**
12.4.2 Rheology **585**
12.4.2.1 Nematic Phases **585**
12.4.2.2 Hexagonal Phases **585**
12.4.2.3 Smectic Phases **586**
12.4.2.4 Cubic Strut Phases **589**
12.5 Summary **590**
References **590**

Chapter 13 Block Copolymers 594
13.1 Introduction **594**
13.2 Thermodynamics of Block Copolymers **596**
13.2.1 The Flory χ Parameter **596**
13.2.2 Microphase Separation and Ordering **598**
13.2.3 Theories for Block-Copolymer Phase Behavior **602**
13.2.3.1 Strong Segregation **603**
13.2.3.2 Weak Segregation **604**
13.2.4 Simulations of Block-Copolymer Phase Behavior **607**
13.3 Rheology and Shear-Aligning of Block Copolymers **607**
13.3.1 Lamellar Microdomains **610**
13.3.1.1 The Linear Modulus **611**
13.3.1.2 Alignment **614**
13.3.1.2.1 Observations **614**
13.3.1.2.2 Explanations **618**

13.3.1.3 Elastic Constants and Defects **623**
13.3.2 Cylindrical Microdomains **624**
13.3.3 Spherical Microdomains **625**
13.3.3.1 Disordered Microdomains **626**
13.3.3.2 Ordered Microdomains **626**
13.4 Summary **629**
References **629**

Appendix: Momentum-Balance Equations in the Absence of Inertia **663**

Common Notation **635**

Author Index **641**

Subject Index **652**