

RHEOLOGY
Principles,
Measurements,
and
Applications

Christopher W. Macosko

I-56081 -579-5 -

1994 VCH Publishers. Inc.

New York

Part I. CONSTITUTIVE RELATIONS 1

1 1 Elastic Solid 5

Christopher W. Macosko

- 1.1 Introduction 5
- 1.2 The Stress Tensor 8
 - 1.2.1 Notation 11
 - 1.2.2 Symmetry 16
 - 1.2.3 Pressure 18
- 1.3 Principal Stresses and Invariants 20
- 1.4 Finite Deformation Tensors 24
 - 1.4.1 Finger Tensor 29
 - 1.4.2 Strain Tensor 32
 - 1.4.3 Inverse Deformation Tensors 32
 - 1.4.4 Principal Strains 34
- 1.5 Neo-Hookean Solid 37
 - 1.5.1 Uniaxial Extension 38
 - 1.5.2 Simple Shear 40
- 1.6 General Elastic Solid 40
 - 1.6.1 Strain-Energy Function 42
 - 1.6.2 Anisotropy 44
 - 1.6.3 Rubber-like Liquids 45
- 1.7 Equations of Motion 45
 - 1.7.1 Mass Balance 45
 - 1.7.2 Momentum Balance 47
- 1.8 Boundary Conditions 52
- 1.9 Summary 58
- 1.10 Exercises 59
- References 62

2 / Viscous Liquid 65

Christopher W. Macosko

- 2.1 Introduction 65
- 2.2 Velocity Gradient 68
 - 2.2.1 Rate of Deformation Tensor 72
- 2.3 Newtonian Fluid 77
 - 2.3.1 Uniaxial Extension 79
- 2.4 General Viscous Fluid 83
 - 2.4.1 Power Law 84
 - 2.4.2 Cross Model 86

2.4.3	Other Viscous Models	86
2.4.4	The Importance of η_{11} ,,	89
2.4.5	Extensional Thickening Models	91
2.5	Plastic Behavior	92
2.5.1	Other Viscoplastic Models	95
2.6	Balance Equations	98
2.6.1	Equations of Motion	99
2.6.2	Boundary Conditions	99
2.6.3	Energy Equation	100
2.6.4	Temperature and Pressure Dependence of Viscosity	100
2.7	Summary	104
2.8	Exercises	105
	References	106

3 / Linear Viscoelasticity 109

Christopher W. Macosko

3.1	Introduction	109
3.2	General Linear Viscoelastic Model	111
3.2.1	Relaxation Spectrum	115
3.2.2	Linear Viscoelasticity in Three Dimensions	115
3.2.3	Differential Form	115
3.3	Small Strain Material Functions	117
3.3.1	Stress Relaxation	118
3.3.2	Creep	119
3.3.3	Sinusoidal Oscillations	121
3.4	Exercises	126

Appendix 3A 127

Robert B. Secor

	Curve Fitting of Relaxation Modulus	127
	Approximating Form	127
	Error Measure	128
	Search Procedures	129
	References	133

4 / Nonlinear Viscoelasticity 135

Ronald G. Larson

4.1	Introduction	135
4.2	Nonlinear Phenomena	138
4.2.1	Normal Stress Difference in Shear	138
4.2.2	Shear Thinning	139
4.2.3	Interrelations Between Shear Functions	140
4.2.4	Extensional Thickening	142

4.3	Simple Nonlinear Constitutive Equations	/46
4.3.1	Second-Order Fluid	/46
4.3.2	Upper-Convected Maxwell Equation	149
4.3.3	Lodge Integral Equation	/53
4.4	More Accurate Constitutive Equations	158
4.4.1	Integral Constitutive Equations	/58
4.4.2	Maxwell-Type Differential Constitutive Equations	/66
4.5	Summary	170
4.6	Exercises	17/
	References	172

Part II. MEASUREMENTS: RHEOMETRY 175

5 / Shear Rheometry: Drag flows 181

Christopher W. Macosko

5.1	Introduction	181
5.2	Sliding Plates, Falling Ball	/84
5.2.1	Falling Cylinder	185
5.2.2	Falling Ball	187
5.2.3	Rolling Ball	/87
5.3	Concentric Cylinder Rheometer	/88
5.3.1	Shear Stress	/90
5.3.2	Shear Strain and Rate	191
5.3.3	Normal Stresses in Couette Flow	/95
5.3.4	Rod Climbing	/98
5.3.5	End Effects	200
5.3.6	Secondary Flows	202
5.3.7	Shear Heating in Couette Flow	203
5.4	Cone and Plate Rheometer	205
5.4.1	Shear Stress	206
5.4.2	Shear Strain Rate	207
5.4.3	Normal Stresses	208
5.4.4	Inertia and Secondary Flow	209
5.4.5	Edge Effects with Cone and Plate	2/3
5.4.6	Shear Heating	2/6
5.4.7	Summary	2/6
5.5	Parallel Disks	2/7
5.5.1	Normal Stresses	22/
5.6	Drag Flow Indexers	222
5.6.1	Rotating Disk in a Sea of Fluid	223
5.6.2	Rotating Vane	224
5.6.3	Helical Screw Rheometer	224
5.6.4	Instrumented Mixers	225
5.7	Eccentric Rotating Geometries	226
5.7.1	Rotating Cantiliver Rod	227

5.7.2	Eccentric Rotating Disks	227
5.7.3	Other Eccentric Geometries	23/
	References	231

6 / Shear Rheometry: Pressure-Driven Flows 237

Christopher W. Macosko

6.1	Introduction	237
6.2	Capillary Rheometer	238
6.2.1	Shear Rate	240
6.2.2	Wall Slip, Melt Fracture	244
6.2.3	True Shear Stress	247
6.2.4	Shear Heating	252
6.2.5	Extrudate Swell	254
6.2.6	Melt Index	256
6.3	Slit Rheometry	257
6.3.1	Normal Stresses	260
6.3.2	Exit Pressure	26/
6.3.3	Pressure Hole	262
6.4	Other Pressure Rheometers	266
6.4.1	Axial Annular Flow	266
6.4.2	Tangential Annular Flow	267
6.4.3	Tilted Open Channel	268
6.4.4	Squeezing Flow	270
6.5	Comparison of Shear Methods	275
6.6	Summary	277
	References	280

7 / Extensional Rheometry 285

Christopher W. Macosko

7.1	Introduction	285
7.2	Simple Extension	288
7.2.1	End Clamps	291
7.2.2	Rotating Clamps	292
7.2.3	Buoyancy Baths	294
7.2.4	Spinning Drop	296
7.3	Lubricated Compression	297
7.3.1	Planar Squeezing	303
7.4	Sheet Stretching, Multiaxial Extension	303
7.4.1	Rotating Clamps	304
7.4.2	Inflation Methods	306
7.5	Fiber Spinning	308
7.5.7	Tubeless Siphon	315
7.6	Bubble Collapse	3/7
7.7	Stagnation Flows	320
7.7.1	Lubricated Dies	322

7.7.2	Unlubricated Dies	322
7.7.3	Opposed Nozzles	323
7.8	Entrance Flows	326
7.9	Summary	332
	References	333

8 / Rheometer Design 337

Christopher W. Macosko

8.1	Introduction	337
8.2	Drag Flow Rheometers	338
8.2.1	Controlled Strain	339
8.2.2	Torque Measurement	342
8.2.3	Normal Stresses	345
8.2.4	Alignment	347
8.2.5	Controlled Stress	349
8.2.6	Environmental Control	352
8.3	Data Analysis	357
8.3.1	Sinusoidal Oscillations	359
8.3.2	Transient	363
8.4	Pressure-Driven Rheometers	364
8.5	Extensional Rheometers	368
8.6	Process Line Rheometers	370
8.7	Summary	373
	References	374

9 / Rheo-Optics: Flow Birefringence 379

Timothy P. Lodge

9.1	Introduction	379
9.2	Review of Optical Phenomena	381
9.2.1	Absorption and Emission Spectroscopies	382
9.2.2	Scattering Techniques	382
9.2.3	Birefringence and Dichroism	384
9.3	Polarized Light	386
9.3.1	Transmission Through a Series of Optical Elements	390
9.4	Flow Birefringence: Principles and Practice	393
9.4.1	The Stress-Optical Relation	393
9.4.2	Range of Applicability of the Stress-Optical Relation	397
9.4.3	Geometries for Measuring Flow Birefringence	400
9.4.4	Birefringence in Steady and Transient Couette Flow	403
9.4.5	Birefringence in Oscillatory Shear Flow	405
9.4.6	Experimental Considerations	407

9.5	Flow Birefringence: Applications	408
9.5.1	Stress Field Visualization	408
9.5.2	Extensional Flow	409
9.5.3	Dynamics of Isolated, Flexible Homopolymers	409
9.5.4	Dynamics of Isolated Block Copolymers	412
9.5.5	Dynamics of Block Copolymer Melts	415
9.5.6	Dynamics of a Binary Blend	415
9.5.7	Birefringence in Transient Flows	416
9.5.8	Rheo-Optics of Suspensions	416
9.5.9	Rotational Dynamics of Rigid Rods	417
9.6	Summary	4/9
	References	419

Part III. APPLICATIONS 423

10 / Suspension Rheology 425

Jan Mewis and Christopher W. Macosko

10.1	Introduction	425
10.2	Dilute Suspensions of Spheres	428
10.2.1	Hard Spheres	428
10.2.2	Particle Migration	430
10.2.3	Emulsions	434
10.2.4	Deformable Spheres	437
10.3	Particle-Fluid Interactions: Dilute Spheroids	439
10.3.1	Orientation Distribution	440
10.3.2	Constitutive Relations for Spheroids	443
10.4	Particle-Particle Interactions	449
10.4.1	Dispersion Forces	450
10.4.2	Electrostatic Forces	451
10.4.3	Polymeric (Steric) Forces	452
10.4.4	Scaling	454
10.5	Brownian Hard Particles	455
10.5.1	Monodisperse Hard Spheres	455
10.5.2	Particle Size Distribution	458
10.5.3	Nonspherical Particles	459
10.5.4	Non-Newtonian Media	460
10.5.5	Extensional Flow of Ellipsoids	460
10.6	Stable Colloidal Suspensions	461
10.6.1	Electrostatic Stabilization	462
10.6.2	Polymeric (Steric) Stabilization	464
10.7	Flocculated Systems	465
10.7.1	Structure in Flocculated Dispersions	465
10.7.2	Static Properties	467
10.7.3	Flow Behavior	468

10.8	Summary	470
	References	47/

11 / Rheology of Polymeric Liquids 475

Matthew Tirrell

11.1	Introduction	475
11.2	Polymer Chain Conformation	476
11.3	Zero Shear Viscosity	479
	11.3.1 Dilute Solution	479
	11.3.2 Nondilute Polymeric Liquids	480
	11.3.3 Coil Overlap	482
11.4	Rheology of Dilute Polymer Solutions	487
	11.4.1 Elastic Dumbbell	487
	11.4.2 Rouse and Other Multihead Models	495
11.5	Concentrated Solutions and Melts	497
	11.5.1 Entanglements	497
	11.5.2 Reptation Model	502
	11.5.3 Effects of Long Chain Branching	505
	11.5.4 Effect of Molecular Weight Distribution	506
11.6	Temperature Dependence	5/0
11.7	Summary	5/2
	References	512

Appendix / Solutions to Exercises

Chapter 1	515
Chapter 2	521
Chapter 3	527
Chapter 4	53/

Index 535