

Contents

Part I Fundamental Principles

1	Preliminary Mathematics	3
1	Vector Space	3
1.1	Definition of Vector Space	3
1.2	Linear Combination and Basis	5
1.3	Dual Space	8
2	Inner Product Space	10
2.1	Generalization of Inner Product	10
2.2	Generalization of Distance	12
2.3	Orthogonalized Basis	13
2.4	Application of Orthogonal Polynomials	20
2.5	Summation Convention	23
3	Coordinate System and Basis	26
3.1	How to Construct a Coordinate System	26
3.2	Cylindrical and Spherical Coordinate Systems	32
3.3	Change of Coordinate Systems	34
4	Vector Analysis	37
4.1	Vector Algebra	37
4.2	Differentiation of Vector	39
4.3	Integration of Vector and Scalar	44
5	Tensor Analysis	54
5.1	Polyadic Notation of Linear Transform	54
5.2	Tensor Algebra	58
5.3	Tensor Calculus	70
6	Fourier and Laplace Transforms	74
6.1	The Dirac Delta Function	75
6.2	Fourier Transform and Its Inversion	78
6.3	Dirac Delta Function Revisited	83
6.4	Laplace Transform and Its Inversion	84
	References	90

2	Continuum Thermomechanics	93
1	Kinematics	94
1.1	Material and Spatial Coordinates	94
1.2	Strain	96
1.3	Deformation of Area and Volume	100
1.4	Rate of Deformation	101
1.5	Relative Deformation Gradient	104
2	Balance Equations	110
2.1	Mass Balance	110
2.2	Momentum Balance	112
2.3	Energy Balance: The First Law of Thermodynamics	118
2.4	Balance Equations in Terms of Flux	121
3	Classical Constitutive Equations	124
3.1	Elasticity	124
3.2	Viscous Fluids	131
3.3	Viscoelastic Models	136
4	Thermodynamics	146
4.1	Equilibrium Thermodynamics	146
4.2	Classical Irreversible Thermodynamics	154
4.3	Theory of Internal Variables	160
5	Principle of Constitutive Equation	166
5.1	Upper-Convective Maxwell Model	166
5.2	Principle of Material Frame Indifference	169
	References	175
3	Statistical Mechanics	177
1	Probability Theory	178
1.1	Moments and Cumulants	179
1.2	Statistical Independence	181
1.3	The Central Limit Theorem	182
1.4	Gaussian Distribution	185
2	Equilibrium Statistical Mechanics	188
2.1	Ensemble Theory	188
2.2	Fluctuations and Equivalence of Ensembles	196
2.3	The Equipartition Theorem and the Virial Theorem	204
3	Brownian Motion	211
3.1	Langevin Equation	211
3.2	Diffusion Equation	214
3.3	Liouville Equation	216
3.4	Generalized Langevin Equation	219
3.5	The Fokker–Planck Equation	223
	References	229

4	Polymer Physics	231
1	Polymer Structure	231
1.1	Definition of Polymer	231
1.2	Structure of a Single Polymer Chain	233
1.3	Structure of Assembly of Polymer Chains	236
2	Chain Conformation and Size of Polymer Chain	239
2.1	Size of Polymer Chain	239
2.2	Chain Models and Universality	242
2.3	Size Distribution	250
2.4	Molecular Weight and Molecular Weight Distribution	254
3	Polymer Solution	260
3.1	Polymer Concentration	260
3.2	Concentration Regimes	261
3.3	Entanglement	264
4	Rubber Elasticity	267
4.1	Thermodynamics of Rubber	268
4.2	Statistical Mechanical Theory	269
4.3	Phenomenological Models	272
	References	280

Part II Linear Viscoelasticity

5	Theory of Linear Viscoelasticity	285
1	Fundamental Theory	285
1.1	The Origin of Viscoelasticity	285
1.2	The Boltzmann Superposition Principle	287
1.3	Dynamic Experiment	293
1.4	The Kramers–Kronig Relations	298
1.5	Thermodynamic Analysis	299
2	Measurement of Linear Viscoelasticity	302
2.1	Devices and Instruments	302
2.2	Preliminary Tests	303
2.3	Inertia Effect in Stress-Controlled Rheometer	310
2.4	Diffusion Wave Spectroscopy	313
3	Phenomenological Models	316
3.1	Spring–Dashpot Models Revisited	316
3.2	Parsimonious Models	321
3.3	Models Based on Fractional Derivatives	327
4	Molecular Theories	332
4.1	Dynamic Equation	332
4.2	The Stress of Polymeric Fluid	337
4.3	The Rouse Model	338
4.4	The Zimm Model	344

4.5	The Doi–Edwards Model	344
4.6	Modification of the Doi–Edwards Model	353
	References	357
6	Numerical Methods	361
1	Polynomial Regression	362
1.1	Basics	362
1.2	Use of Orthogonal Polynomials.	363
1.3	B-Spline Regression	366
2	Nonlinear Regression	369
2.1	Basics	369
2.2	The Levenberg–Marquardt Algorithm	370
2.3	Example I	371
2.4	Example II	374
3	Padé Approximation.	377
3.1	Basics	377
3.2	Application to the FENE Model	379
3.3	Application to Discrete Spectrum	380
4	Numerical Integration and Differentiation	382
4.1	Error Analysis of Integration of Experimental Data	383
4.2	Numerical Differentiation with Regularization	385
5	Discrete Fourier Transform	392
5.1	Fourier Series	392
5.2	Discrete Fourier Transform.	393
	References	395
7	Viscoelastic Spectrum	397
1	Fundamentals	397
1.1	Importance of Spectrum	397
1.2	The Fuoss–Kirkwood Relations.	398
1.3	Ill-Posedness of Spectrum	406
1.4	Some Important Equations and Inequalities.	408
2	Algorithms for Continuous Spectrum	411
2.1	Regularization Method.	411
2.2	Fixed-Point Iteration	414
2.3	Power Series Approximation.	416
2.4	Other Algorithms	422
2.5	Comparison of Algorithms	425
3	Algorithms for Discrete Spectrum	427
3.1	Nonlinear Least Squares.	427
3.2	The Padé–Laplace Methods	429
3.3	Approximation from Continuous Spectrum.	430
	References	434

8	Time-Temperature Superposition	437
1	Fundamentals of TTS	437
1.1	Phenomenology of TTS	437
1.2	Temperature Dependence of Shift Factor	442
1.3	Molecular Explanation of TTS	445
2	Geometric Interpretation	447
2.1	Geometric Analogy to TTS	447
2.2	New Master Curve	448
2.3	Application of Numerical Differentiation	452
3	Algorithms for TTS	454
3.1	Nonlinear Regression Method	454
3.2	Minimization of Arc Length	455
	References	456
9	Applications to Polymer Systems	459
1	Interconversion of Various Experimental Data	459
1.1	Static Data to Dynamic Data	459
1.2	Laplace Transform from Dynamic Data	467
2	Polymer Melts and Solutions	468
2.1	Monodisperse Linear Polymer in Molten State	468
2.2	Polydisperse Polymer Melts	473
2.3	Polymer Solution	477
3	Immiscible Blend of Polymers	479
3.1	Mixture of Newtonian Fluids	480
3.2	The Gramespacher and Meissner Model	481
3.3	The Palierne Model	483
3.4	Comparison of the GM and the Palierne Models	483
	References	485

Part III Nonlinear Viscoelasticity

10	Nonlinear Constitutive Equations	491
1	Rheometrics	491
1.1	Shear Flow	492
1.2	Measurement of Steady Viscoelastic Functions	496
1.3	Simple Elongational Flow	505
2	Models Based on Expansion	508
2.1	Rivlin-Ericksen Expansion	508
2.2	Green-Rivlin Expansion	510
3	Generalization of Linear Viscoelastic Models	513
3.1	Oldroyd Generalization	513
3.2	K-BKZ Model	516

4	Models Based on Speculation of Structure	521
4.1	Spring-Dumbbell Models	521
4.2	Temporary Network Approaches	532
4.3	Multimode Versions	534
5	Thermodynamic Theory	537
5.1	Leonov Model	537
5.2	Thermodynamic Analysis of Other Models	541
	References	542
11	Large Amplitude Oscillatory Shear	545
1	Introduction to LAOS	545
1.1	Phenomenology of LAOS	545
1.2	Overview of LAOS Research	546
2	Methods of Analysis	549
2.1	FT-Rheology	549
2.2	Stress and Strain Decomposition	553
2.3	Scaling Theory of LAOS	563
3	Analytical Solution of LAOS	571
3.1	Convected Maxwell Models	572
3.2	Time-Strain Separable K-BKZ Model	582
3.3	Nonseparable Maxwell Models	583
4	Semi-analytical Method for LAOS	592
	References	597
	Appendix: Functional Derivative	601
	Index	609