

2nd Edition

Rheology for Chemists

An Introduction

Jim W Goodwin and Roy W Hughes



RSC Publishing



Instituto Nacional
de Tecnología Industrial
Extensión y Desarrollo
División Bibliotecas

Rheology for Chemists

An Introduction

2nd Edition

Jim W Goodwin

Invitrogen Corporation, Eugene, Oregon, USA

Roy W Hughes

Bristol Colloid Centre, University of Bristol, UK

RSC Publishing

Contents

Chapter 1 Introduction

1.1	Definitions	2
1.1.1	Stress and Strain	2
1.1.2	Rate of Strain and Flow	4
1.2	Simple Constitutive Equations	5
1.2.1	Linear and Nonlinear Behaviour	5
1.2.2	Using Constitutive Equations	6
1.3	Dimensionless Groups	6
1.3.1	The Deborah Number	7
1.3.2	The Péclet Number	8
1.3.3	The Reduced Stress	9
1.3.4	The Taylor Number	10
1.3.5	The Reynolds Number	11
1.4	Macromolecular and Colloidal Systems	12
	References	13

Chapter 2 Elasticity: High Deborah Number Measurements

2.1	Introduction	14
2.2	The Liquid-Solid Transition	16
2.2.1	Bulk Elasticity	18
2.2.2	Wave Propagation	19
2.3	Crystalline Solids at Large Strains	22
2.3.1	Lattice Defects	23
2.4	Macromolecular Solids	25
2.4.1	Polymers – An Introduction	26
2.4.2	Chain Conformation	26
2.4.3	Polymer Crystallinity	31
2.4.4	Crosslinked Elastomers	34
2.4.5	Self-associating Polymers	36
2.4.6	Noninteractive Fillers	40

2.4.7	Interactive Fillers	42
2.4.8	Summary of Polymeric Systems	44
2.5	Colloidal Gels	44
2.5.1	Interactions Between Colloidal Particles	44
2.5.2	London-van der Waals' Interactions	45
2.5.3	Depletion Interactions	46
2.5.4	Electrostatic Repulsion	47
2.5.5	Steric Repulsion	48
2.5.6	Electrosteric Interactions	50
	References	52

Chapter 3 Viscosity: Low Deborah Number Measurements

3.1	Initial Considerations	55
3.2	Viscometric Measurement	58
3.2.1	The Cone and Plate	59
3.2.2	The Couette or Concentric Cylinder	60
3.3	The Molecular Origins of Viscosity	63
3.3.1	Flow of Gases	63
3.3.2	The Flow of Liquids	64
3.3.3	Density and Phase Changes	65
3.3.4	Free-volume Model of Liquid Flow	67
3.3.5	Activation-energy Models	70
3.4	Superfluids	71
3.5	Macromolecular Fluids	72
3.5.1	Colloidal Dispersions	72
3.5.2	Dilute Dispersions of Spheres	72
3.5.3	Concentrated Dispersions of Spheres	75
3.5.4	Shear-thickening Behaviour in Dense Suspensions	80
3.5.5	Charge-stabilised Dispersions	81
3.5.6	Dilute Polymer Solutions	87
3.5.7	Surfactant Solutions	89
	References	90

Chapter 4 Linear Viscoelasticity I: Phenomenological Approach

4.1	Viscoelasticity	92
4.2	Length and Timescales	93
4.3	Mechanical Spectroscopy	94
4.4	Linear Viscoelasticity	95
4.4.1	Mechanical Analogues	96
4.4.2	Relaxation Derived as an Analogue to 1 st -order Chemical Kinetics	98

4.4.3	Oscillation Response	100
4.4.4	Multiple Processes	104
4.4.5	A Spectral Approach to Linear Viscoelastic Theory	108
4.5	Linear Viscoelastic Experiments	111
4.5.1	Relaxation	113
4.5.2	Stress Growth	115
4.5.3	Antithixotropic Response	116
4.5.4	Creep and Recovery	117
4.5.5	Strain Oscillation	119
4.5.6	Stress Oscillation	121
4.6	Interrelationships Between the Measurements and the Spectra	122
4.6.1	The Relationship Between Compliance and Modulus	123
4.6.2	Retardation and Relaxation Spectrum	125
4.6.3	The Relaxation Function and the Storage and Loss Modulus	126
4.6.4	Creep and Relaxation Interrelations	126
4.7	Applications to the Models	127
4.8	Microstructural Influences on the Kernel	130
4.8.1	The Extended Exponential	130
4.8.2	Power Law or the Gel Equation	131
4.8.3	Exact Inversions from the Relaxation or Retardation Spectrum	132
4.9	Nonshearing Fields and Extension	132
	References	134

Chapter 5 Linear Viscoelasticity II: Microstructural Approach

5.1	Intermediate Deborah Numbers $D_e \approx 1$	135
5.2	Hard Spheres and Atomic Fluids	136
5.3	Quasihard-sphere Dispersions	137
5.3.1	Quasihard-sphere Phase Diagrams	138
5.3.2	Quasihard-sphere Viscoelasticity and Viscosity	142
5.4	Weakly Attractive Systems	147
5.5	Charge-repulsion Systems	155
5.6	Simple Homopolymer Systems	165
5.6.1	Phase Behaviour and the Chain Overlap in Good Solvents	165
5.6.2	Dilute Solution Polymers	172
5.6.3	Undiluted and Concentrated Nonentangled Polymers	175

5.6.4	Entanglement Coupling	176
5.6.5	Reptation and Linear Viscoelasticity	178
5.7	Polymer Network Structures	184
5.7.1	The Formation of Gels	184
5.7.2	Chemical Networks	186
5.7.3	Physical Networks	187
	References	192

Chapter 6 Nonlinear Responses

6.1	Introduction	194
6.2	The Phenomenological Approach	195
6.2.1	Flow Curves: Definitions and Equations	195
6.2.2	Time Dependence in Flow and the Boltzmann Superposition Principle	198
6.2.3	Yield Stress Sedimentation, and Linearity	204
6.3	The Microstructural Approach – Particles	208
6.3.1	Flow in Hard-sphere Systems	208
6.3.2	The Addition of a Surface Layer	211
6.3.3	Aggregation and Dispersion in Shear	212
6.3.4	Weakly Flocculated Dispersions	215
6.3.5	Strongly Aggregated and Coagulated Systems	221
6.3.6	Long-range Repulsive Systems	226
6.3.7	Rod-like Particles	230
6.4	The Microstructural Approach – Polymers	235
6.4.1	The Role of Entanglements in Nonlinear Viscoelasticity	235
6.4.2	Entanglement of Solution Homopolymers	238
6.4.3	The Reptation Approach	239
6.5	Novel Applications	245
6.5.1	Extension and Complex Flows	245
6.5.2	Uniaxial Compression Modulus	249
6.5.3	Deformable Particles	252
	References	256

Subject Index

258

Subject Index

Note: page numbers in *italics* refer to figures.

- activation energy
 - diffusion 25
 - flow model 70-1
- aggregation 221-6
 - diffusion-limited 225
 - and dispersion in shear 212-15
 - flocculation 215-21
 - rate-limited 225
- anchor groups 49
- anisotropic systems 232
- annealing 25
- antithixotropic response 116-17, 199
- Arrhenius equation 6-7
- associative thickeners 36, 189-90
- atomic fluids 136-7
- attapulgite 233-4

- Barker-Henderson perturbation 150-1
- bead-spring model 172
- Beer-Lambert law 94
- bimodal dispersions 76-9
- Bingham plastic 5, 6, 195-6
 - viscometric measurement 62-3
- Bingham yield 153, 208, 215-16, 218, 219, 222
- Boltzmann function 5
- Boltzmann superposition principle 111-12
 - applications 113-22, 198-204
- Bragg diffraction 141-2
- Burger body 118

- Casson equation 195, 219-21
- cellulose ethers 37
- chain, polymer
 - chain-overlap parameter 165, 238-9
 - and physical networks 189-99
 - conformation 26-31, 86, 108
 - entanglement *see* entanglement
 - expansion factor 168-70
 - length 28, 166, 168, 172
 - radius of gyration 29
- charge-repulsion/stabilisation 81-7, 155-65
 - nonlinear long-range 226-30
- chemical networks 184, 186-7
- clays 87, 204, 221-4
 - rod-like particles 233-4
- coagulated systems 221-6
 - application of shear 212-15
- collision diameter 17
- collision trajectories 83
- colloidal dispersions 72
 - aggregation/coagulation 221-6
 - application of shear 212-15
 - weak flocculation 215-21
 - bi and trimodal systems 77-8
 - charge-stabilised 81-7, 155-65
 - nonlinear long range 226-30
 - electroviscous effects 82-7, 88
 - hard sphere models
 - concentrated 75-9
 - dilute 72-5
 - sedimentation 204-7

- shear-thickening 80-1, 195, 196-7, 212
- shear-thinning 5-6, 78-9, 188, 195, 196-7
- surfactant solutions 89-90
- weakly attractive systems 147-55
- yield stress 196, 204-7
- colloidal gels 44-5
 - 'colloidal springs' 52
 - depletion interactions 46-7
 - diffusional timescales 12
 - electrostatic repulsion 47-8
 - electrosteric interactions 50-2
 - London-van der Waals interactions 44-5
 - steric repulsion 48-50
- complex modulus 101-2, 104, 124
- compliance
 - bulk 18
 - complex 104
 - creep 117
 - defined 14, 112
 - glassy 117
 - of polymer 32
 - relationship with modulus 123-5
 - steady state 122
- compressibility 8
 - osmotic 140
- compression modulus 249-51
- compressional wave 20, 22
- compressive stress 2
- concentric cylinder rheometer 59, 60-3
- cone and plate rheometer 11, 59-60, 59
- conformation 26-31, 86, 108
- constitutive equations 5-6, 57
 - Bingham plastic 62
 - viscoelastic modelling 96, 101
- continuum modelling 46
- coordination number 151-2, 155-6
- copolymers 36
- Couette rheometer 10-11, 59, 60-3
- Cox-Merz rule 198
- creep
 - rate 24
 - recovery 117-19
 - relaxation 126-7
 - see also* compliance
- critical micelle concentration 89
- Cross model 195, 196, 202
- crosslinks *see* network structures
- crystalline solids 22-3
 - lattice defects 23-5
- crystallinity, polymer 31-4
- crystallisation 65, 66
- crystallites 32, 34
- cup and bob viscometer 56
- dashpots and springs 94-6
- Deborah Number 7-8
 - high (elasticity) 14-16
 - intermediate (viscoelasticity) 92-3, 135-6
 - low (viscosity) 55-8
 - nonlinear systems 195
 - and superfluids 71
- Debye length 85
- deformable particles 252-6
- dense random packing 41
- density changes 65-7
- depletion interactions 46-7
- diffusion 10, 161-2
 - coefficient 8, 93
 - self-diffusion 16, 17
 - ionic solid 25
 - modes 16
 - timescales 12
- dilatancy 80, 198
- dimensionless groups 6-12
 - energy density 155, 156
 - internal energy 157
- Dirac delta function 128-9, 132, 156
- dislocations 23-4
- dispersions *see* colloidal dispersions
- Doi-Edwards model 239, 243-5
- double gap rheometer 59
- dynamic modulus 124
- dynamic yield stress 6
- effective medium approach 41, 76
- Einstein-Smoluchowski equation 8
- elastic limit 22, 23
- elastic modulus 2
 - bulk 18, 19, 22

- estimated by wave velocity 21
 - for hydrogel beam 32, 33
 - Young's modulus defined 2
- elasticity 14-16
- elastomers 4-6, 15, 34-6
- electrical double layer 47
- electrostatic repulsion 47-8, 49
- electrosteric interactions 50-2
- electroviscous effects 82-7, 88
- elongational hardening 248
- emulsions 252-6
 - drop viscosity 73
- entanglement, polymer chain 170-2, 176-8
 - mesh and tube models 181
 - nonlinear viscoelasticity 235-8
 - see also* reptation
- excluded volume 76, 82
- exponential kernel, extended 130-2
- extension
 - nonshearing fields 132-3
 - stress 2
 - viscosity 4, 133
- extensional flow 4-5, 245-9
- face-centred cubic packing 136-7
- fillers
 - interactive 42-3
 - noninteractive 40-2
- flocculation 215-21
 - see also* aggregation
- Flory-Fox parameter 88
- Flory-Huggins theory 29-30
- flow 4-5
 - extensional 4-5, 245-9
 - flow field dilation 72-3
 - gas 63-4
 - plastic 23, 198-9
 - stable secondary 11
 - time dependence in 198-204
 - see also* liquid flow
- flow curves 195-8, 199
- fluidity defined 55
- fractal model 224-6
- fragile glass 160
- free-volume model 67-70
- freezing 16-19
- Frenkel defects 23
- gas flow 63-4
- gas, ideal 136
 - diffusion coefficient 93
 - equation 18
- gel emulsion 252-3
- gel equation 131-2
- gel point 185
- gels
 - colloidal *see* colloidal gels
 - polymer *see* network structures
- Gibbs free energy 139
- glasses 160
- glycerol 18, 19, 66, 67
- Graessley model 236-8, 243-4
- grain boundaries 24
- Hamaker constant 45
- hard/quasihard-sphere approaches 136-8
 - charge-repulsion systems 155-65
 - homopolymers 165-6
 - phase diagrams 138-42
 - typical experimental models 208
- viscoelasticity 136-7, 142-6
 - nonlinear 208-11
- viscosity 142-6
 - concentrated dispersions 75-9
 - dilute dispersions 72-5
 - weakly attractive systems 147-55
- heat capacity 18, 19
- helium 71
- Helmholtz free energy 139-40, 151
- HEUR polymers 37, 38, 42
- hexadecyl trimethyl ammonium salicylate 89-90
- high internal phase emulsion 252-3
- HMHEC polymers 37, 38-9
- honey 66
- Hookean solid 5, 14
- Hookean springs 94
- Hooke's Law 2, 14, 95
 - simple harmonic motion 20
- HPAM polymers 37
- Huggins coefficient 88, 166

- hydrodynamic interactions 74–5
 - hard-sphere dispersion 165
- hydrodynamic size 87
- hydrogels 32–4
- hydrogen bonding 36
- hydrophobic polymers 36–7, 189–90

- internal energy density 152
- intrinsic viscosity 165
- ionic crosslinks 190, 191–2
- isothermal bulk modulus 140

- jump diffusion 25, 161–2

- kaolin 87, 222–3
- Kelvin–Voigt model 96–7
 - creep and recovery 117–19
 - retardation spectrum 109, 129
- kernel, extended exponential 130–2
- Kerr effect 231–2, 233
- Kohlrausch law 160
- Krieger model 195, 196, 208
- Krieger–Dougherty expression 143, 202, 215, 222

- Laplace transformation 127
- lattice
 - defects 23–5, 161
 - packing 155
- lead metal 92
- Lennard–Jones–Devonshire equation 17, 46
- light scattering 140–2, 144
- linear viscoelasticity 7, 92–4, 111–13, 135–6
 - data transform/function
 - interrelationships 127–9
 - modelling
 - hard/quasihard-sphere approach 136–42
 - mechanical analogues 95–7
 - spectral approaches 94–5, 100, 108–11, 122–3
- liquid
 - Newtonian 4, 5, 55, 56
 - superfluid 71
 - viscoelastic 105–6, 109, 115, 119
- liquid flow 4–5, 64–6
 - activation energy models 70–1
 - density and phase changes 65–7
 - energy changes 57
 - free-volume model 67–70
 - superfluids 71
- liquid-like behaviour 7
- liquid–solid transition 16–17
- London–van der Waals interactions 44–5
- longitudinal bulk modulus 22
- loss modulus 110, 111, 125, 126

- macromolecular systems 12, 25–6, 72
- Madelung constant 19
- Margules equation 61
- Maxwell model 96–7
 - dashpots and springs 94–6
 - multiple processes/models 104–8
 - oscillation response 100–4
 - and transform of data 127–9
- mechanical spectroscopy 94–5, 100, 108–11, 122–3
- melting 16–19, 65–6
- memory function 112–13
- metals
 - lead 92
 - stress–strain curve 22–3
- micelles 89
- microgels 252
- molecular weight 167, 170, 175–6
- monosaccharides 66
- Mooney rheometer 59, 61–2

- neo-Hookean model 14
- network modulus 35, 39
- network structures 184
 - chemical networks 186–7
 - gel formation 184–6
 - network defects 38–40
 - physical networks 187–92
- Newtonian dashpots 94
- Newtonian fluid 4, 5
 - constitutive equation 57
 - defined 55, 56
 - viscometric measurements 60–2

- Newtonian plateaus 196
- nonlinear responses 5-6, 194-5
- colloidal systems
 - aggregated 211-21
 - long-range repulsive 226-30
 - rod-like particles 230-5
 - emulsions 252-6
 - flow
 - extensional/ complex 245-9
 - flow curves 195-8
 - in hard-sphere systems 208-11
 - time dependent 198-204
 - polymer entanglement 235-9
 - and reptation 239-45
 - sedimentation 204-7
 - uniaxial compression modulus 249-51
- nonshearing fields 132-3
- nontangled polymers 175-6
- order-disorder transition 137, 155
- oscillation response 95, 100-4
 - strain 119-21, 123-4
 - stress 121-2, 123-4
- osmotic compressibility 140
- osmotic pressure
 - and depletion potential 47
 - dilute polymer solution 30
 - quasihard-sphere dispersions 138, 139, 140, 141
 - and yield stress 218
- pair distribution function 147-8, 151, 153, 154-5
- pair potentials
 - colloidal 44, 46, 48, 49, 51
 - Lennard-Jones-Devonshire 17
 - polystyrene particles 149-50
 - quasihard-sphere dispersions 138
 - titanium dioxide in ethylene glycol 81-2
- pair-interaction curve 213
- Péclet Number 8-9
 - in concentrated dispersion 79
 - and nonlinear responses 194
 - and rod-like particles 231
- phase behaviour, polymer 165-72
- phase changes 16-19, 65-7, 68
- phenomenological approach 92-3
- physical gels 35
- physical networks 184, 187-92
- Pickering emulsions 252
- plastic/pseudoplastic materials
 - defined 195, 196
 - flow 23, 198-9
 - sedimentation and yield stress 204-7
 - stress/strain behaviours 197, 198, 203
- Poisson's ratio 16, 133
- poly(acrylamides) 37, 189
- poly(acrylic acid) 86, 87, 88
- polybutadiene 169-70, 171
- poly(dimethyl siloxane) 185
- polydispersion 236-7, 245
- polyelectrolytes 50, 86-7, 88
- poly(ethylene glycol) 28, 37
- poly(ethylene oxide) 28, 29, 37
- polyisoprene 218-19
- polymers 26, 165-92
 - bead-spring model 172
 - chain *see* chain
 - colloidal dispersions 86-9
 - concentrations defined 30-1, 87
 - conformation 26-31, 86, 108
 - crystallinity 31-4
 - depletion interactions 46
 - elastomers 4-6, 15, 34-6
 - entangled *see* entanglement
 - fillers
 - interactive 42-3
 - noninteractive 40-2
 - hydrodynamic size 87
 - nontangled 173-5
 - phase behaviour 165-72
 - polymer coils 166-8
 - polymer 'springs' 32, 34-5
 - reptation *see* reptation
 - self-associating 36-40
 - in solution
 - concentrated 175-6, 238-9
 - dilute 168, 173-5
 - summary of systems 44
 - see also* network structures
- poly(methyl methacrylate) 208, 209

- poly(methylacrylate) 138
- polystyrene particles 51
- polystyrene-latex 85, 87, 149–50, 161–2, 164
- poly(tetrafluoroethene) 233, 233
- poly(vinyl acetate) 190, 191, 192
- poly(vinyl alcohol) 32, 33
- poly(vinylidene fluoride) 228, 229
- power law 6
 - fluids 196
 - gel equation 131–2
- pressure 2
- proteins 50
- pseudoplastic *see* plastic

- quasihard-sphere *see* hard/quasihard-sphere

- random walk 27–8
- rate equation 7
- reduced stress 9–10
- relaxation 135
 - concentrated charge dispersions 159
 - and creep interrelations 126–7
 - experiments 112, 113–15
 - as first order rate process 98–101
 - modelling 98–9, 106
 - structural 143–6
- relaxation function 112, 126
 - charge-repulsion systems 164–5
 - entanglement 176
 - and storage/loss modulus 126
 - transform of 127–8
 - viscoelastic liquid 109
- relaxation spectrum 109–11, 125–6
 - charge-repulsion systems 162–4
 - Dirac delta function 128–9, 132, 156
 - exact inversion 132
 - rules for modelling 129
- relaxation time 7–8
 - and elasticity 14
 - and Maxwell model 105–7
 - structural of liquid 94
- reptation 34, 181
 - and linear viscosity 178–84
 - nonlinear responses 239–45
- repulsion *see* charge–repulsion
- residence time 247
- resonance, sample 114
- retardation spectrum 109, 125–6
 - exact inversion 132
 - rules for modelling 129
- Reynolds Number 11–12, 58
- rheograms 14–15
 - Bingham plastic 63
 - elastomer 15
 - water 55, 56
- rheology defined 1
- rheometers 56, 58, 59
- rheopexy 198
- rigidity 14
 - modulus 14–15, 16
- rod-like particles 230–5
- Rouse model 172–3, 174, 175, 177

- Schottky defects 23
- sedimentation 204–7, 249–51
- self-associating polymers 36–40
- self-diffusion coefficient 16, 17
- shear
 - defined 2, 3
 - rate 4
- shear wave 20, 22
- shear-thickening 80–1, 195, 196–7, 212
- shear-thinning 5–6, 78–9, 188, 195, 196–7
- silica dispersions 138, 207, 208, 209, 229
- 'Silly Putty' 8
- simple harmonic motion 20–1
- solid
 - Hookean 5, 14
 - viscoelastic 106–7, 107, 108, 116
- solid-like behaviour 7, 14, 155
- spectral approach *see* mechanical spectroscopy
- spectroscopy 94
- spraying 4
- spreading 4
- springs and dashpots 94–6
- state, change of 16–19, 65–7
- steric repulsion 48–50
- Stokes drag 84
- Stokes–Einstein equation 8, 93

storage modulus 110, 111, 125, 126

strain

- defined 2
- hardening/softening 3
- instantaneous 113
- oscillation 95, 119–21, 123–4
- rate of 4–5

stress

- defined 2, 3
- growth 115–16
- oscillation 95, 121–2, 123–4
- overshoot 203, 243, 244, 249
- relaxation *see* relaxation

stress-strain-time relationship 5–6

structure factor 144–5, 147, 149

supercooled liquid 67

superfluids 71

superposition principle 111

surface layers 211–12

surfactant solutions 89–90

suspensions *see* colloidal dispersion

Taylor Number 10–11

Taylor vortices 11

tensors 3

terminal zone 176

tetrachloromethane 69

thermodynamics 138–40

thickeners 12

- associative 36
- and depletion interactions 46

thixotropy 199

- loop 202–4

time-dependent flow 198–204

timescales

- diffusional 12
- linear viscosity 92, 93–4
- observational 7–8

titanium dioxide dispersion 81

transient crosslinks 188–9, 190, 191

transition zone 176

trimodal dispersion 76–9

Trouton ratio 133

turbulent flow 11, 12

uniaxial compression modulus 249–51

vaporisation 64

velocity gradient 4, 55

viscoelastic fluid 105–6, 109, 115, 119

viscoelastic solid 106, 107, 108, 116

viscoelasticity *see* linear viscoelasticity

viscometric measurement 58–63

- cone and plate 11, 59–60
- Couette or concentric cylinder 10–11, 59, 60–3
- rheometer geometries 56, 58, 59
- shear-thinning behaviour 5–6

viscosity 7, 55–8

- coefficient of 4, 55
- dynamic 104
- as function of volume fraction 153, 154
- intrinsic 73, 166
- molecular origins of 1, 63
- quasihard-sphere approach 72–9, 142–6

viscosity modifiers 12, 36

viscous flow *see* flow

Voigt model *see* Kelvin–Voigt

Volterra integral equation 126

volume fraction 153, 154, 157

water 55, 56

wave propagation 19–22

work-hardening 23, 24

yield stress 196, 204–7

- Bingham 153, 208, 215–16, 218, 219, 222

Young's modulus *see* elastic modulus

Zimm model 172, 174–5, 177