

Contents

Preface	<i>page</i> xiii
General list of symbols	xvi
Useful physical constants and values	xx
1 Introduction to colloid science and rheology	1
1.1 Colloidal phenomena	1
1.1.1 Forces acting on individual colloids	2
1.1.2 Colloidal interactions	6
1.1.3 Phase behavior and colloidal stability	15
1.2 Principles of rheology	18
1.2.1 Basic concepts	18
1.2.2 Generalized Newtonian fluids	24
1.2.3 Viscoelasticity	25
1.2.4 Application to colloidal dispersions	30
A look ahead	32
Appendix: Second virial coefficients	32
Chapter notation	33
References	34
2 Hydrodynamic effects: Non-colloidal particles	36
2.1 Introduction	36
2.2 Landmark observations	37
2.2.1 Summary	40
2.3 Dilute systems	41
2.3.1 Flow around and motion of single particles	41
2.3.2 Viscosity of dilute suspensions	43
2.3.3 Summary	46
2.4 Semi-dilute suspensions	46
2.4.1 Summary	51
2.5 Concentrated suspensions	51
2.5.1 Microstructure	52
2.5.2 Viscosity	54
2.5.3 Other stress components	60

viii **Contents**

2.5.4 Summary	62
2.6 Other flow phenomena	63
2.6.1 Diffusion or migration	63
2.6.2 Inertial effects	67
2.6.3 Sedimentation	68
2.6.4 Summary	69
Appendix A: Derivation of Einstein expression for intrinsic viscosity	70
Appendix B: Derivation of phenomenological equations for suspension viscosity	71
Chapter notation	72
References	73
3 Brownian hard spheres	80
3.1 Introduction	80
3.2 Landmark observations	81
3.3 Structure and thermodynamic properties of the hard sphere fluid	85
3.3.1 Pressure in a hard sphere fluid	86
3.3.2 Brownian forces in concentrated dispersions	87
3.4 Rheology of dilute and semi-dilute dispersions	90
3.5 Concentrated dispersions	95
3.5.1 Zero shear viscosity	95
3.5.2 Linear viscoelasticity	101
3.5.3 Steady shear rheology	105
3.5.4 Hard sphere colloidal glass transition and mode-coupling theory	109
Summary	112
Appendix A: Principles of the Smoluchowski equation for dispersion micromechanics	113
Appendix B: The role of hydrodynamic interactions	114
Appendix C: Osmotic pressure for a hard sphere solid	115
Chapter notation	116
References	116
4 Stable systems	122
4.1 Introduction	122
4.2 Landmark observations	123
4.3 Electrostatically stabilized systems	127
4.3.1 Dilute and semi-dilute suspensions	127
4.3.2 Concentrated suspensions	131
4.4 Sterically stabilized systems	137
4.4.1 Mechanism	137
4.4.2 Dilute systems	138
4.4.3 Non-dilute systems	139
4.5 Electrosterically stabilized systems	147

Contents**ix**

Summary	149
Chapter notation	149
References	150
5 Non-spherical particles	155
5.1 Introduction	155
5.2 Landmark observations	155
5.3 Particle motion	160
5.4 Rheology of dilute suspensions of non-spherical particles	163
5.5 Semi-dilute suspensions of non-spherical particles	167
5.6 Concentrated suspensions of non-spherical particles	168
5.7 Charged non-spherical particles	172
Summary	173
Appendix: Structural description of the stresses in fiber suspensions	173
Chapter notation	175
References	176
6 Colloidal attractions and flocculated dispersions	180
6.1 Introduction	180
6.1.1 Methods to induce interparticle attraction and flocculation	181
6.2 Landmark observations	183
6.3 Phase behavior, microstructure, and state diagrams	187
6.3.1 Equilibrium phase behavior	187
6.3.2 Flocs and fractals	188
6.3.3 Effect of flow on floc structure	190
6.3.4 Stable clusters	193
6.3.5 Percolation, gelation, jamming, and vitrification	193
6.4 Rheology at low volume fractions	201
6.5 Concentrated dispersions	203
6.6 Rheology of gelled systems	206
6.6.1 Moduli and yield stress of gels	207
6.7 Kinetics of aggregating systems	214
6.8 Polymer bridge flocculation	214
Summary	215
Appendix: Influence of weak attractions on near hard sphere dispersion rheology	216
Chapter notation	217
References	218
7 Thixotropy	228
7.1 Introduction	228
7.2 The concept of thixotropy	228
7.2.1 Definition	228
7.2.2 Thixotropy versus viscoelasticity	230
7.3 Landmark observations	231

x **Contents**

7.4	Rheological phenomena	232
7.4.1	Start-up and intermittent flows	232
7.4.2	Hysteresis loops	234
7.4.3	Stepwise changes in shear	235
7.4.4	Creep tests	236
7.4.5	Oscillatory flow	237
7.5	Constitutive equations	239
7.5.1	Structure kinetics models	239
7.5.2	Integral models	244
	Summary	245
	Appendix: Parameter estimation and model assessment	245
	Chapter notation	248
	References	248
8	Shear thickening	252
8.1	Introduction	252
8.2	Landmark observations	253
8.3	Shear thickening colloidal dispersions	261
8.3.1	Dilute dispersions	261
8.3.2	Concentrated dispersions	265
8.3.3	Non-spherical particle dispersions	274
8.3.4	Extensional thickening, confinement, and field effects	275
8.3.5	Elastohydrodynamic limit of shear thickening	277
8.3.6	Models for predicting the onset of shear thickening	278
8.4	Dilatancy and shear thickening in suspensions	281
	Summary	283
	Chapter notation	284
	References	284
9	Rheometry of suspensions	291
9.1	Introduction	291
9.2	Basic measurement geometries	291
9.2.1	Cone and plate	292
9.2.2	Parallel disks	292
9.2.3	Coaxial cylinders	293
9.2.4	Capillary flow	294
9.3	Measurement problems and basic procedures	295
9.3.1	Measurement problems	295
9.3.2	Selection of measurement geometry	297
9.3.3	General measurement procedures	299
9.4	Specific measurement procedures	300
9.4.1	Wall slip	300
9.4.2	Yield stress (shear)	305
9.4.3	Compressive yield stress	313
9.4.4	Thixotropy	315
9.4.5	Large amplitude oscillatory shear flow (LAOS)	316

Contents

xi

Appendix: Characterization of wall slip	318
Chapter notation	319
References	320
10 Suspensions in viscoelastic media	325
10.1 Introduction	325
10.2 Landmark observations	326
10.3 Particle motion	329
10.4 Rheological behaviour of dilute suspensions	335
10.5 Rheological behavior of concentrated suspensions	336
10.5.1 Steady state shear flow	337
10.5.2 Dynamic moduli	340
10.5.3 Relaxation function	341
10.5.4 Uniaxial extensional flow	341
10.5.5 Fiber suspensions	341
10.5.6 Filled polymer melts and nanocomposites	343
Summary	346
Chapter notation	347
References	347
11 Advanced topics	354
11.1 Special methods for bulk rheometry	354
11.1.1 Stress jumps	354
11.1.2 Superposition moduli	355
11.2 Microrheology	357
11.2.1 Passive microrheology	359
11.2.2 Active microrheology	360
11.2.3 Nonlinear microrheology	361
11.2.4 Concluding remarks	364
11.3 Field-response systems: Electrorheological and magnetorheological suspensions	365
11.3.1 Electrorheological fluids	365
11.3.2 Magnetorheological fluids	371
11.4 Two-dimensional colloidal suspensions	373
11.4.1 Interactions and structure in 2D suspensions	374
11.4.2 Interfacial rheometry	376
11.4.3 Rheological properties of 2D suspensions	378
11.4.4 Flow visualization using 2D suspensions	380
Chapter notation	381
References	382
Index	388