## CONTENTS

	Frontispiece	
	Preface	xiii
	Units and physical constants	xvi
	Mathematical symbols	XV111
1	A Survey of Colloidal Dispersions	1
1.1	Colloidal phenomena	1
1.2	Historical notes	7
1.3	Recent developments	9
1.4	The classification of colloids	12
1.5	An overview	14
	References	18
2	Hydrodynamics	21
2.1	Introduction	21
2.2	Description of the motion of continuous media	22
2.3	Two simple flow fields	25
	Steady laminar shear	25
	Potential flow past a sphere	28
2.4	Characteristics of Stokes flow	30
2.5	Singular solutions to the Stokes equations	31
2.6	Dynamics of isolated spheres	35
2.7	Unsteady translation of spheres	42
2.8	Two spheres translating through a quiescent fluid	44
2.9	Two spheres in a shear flow	53
2.10	Summary	60
	References	62
	Problems	63
3	Brownian Motion	65
31	Introduction	65
3.1	The Langevin equation	66
3.3	Brownian motion and diffusion	68

3.4	Measurement by photon correlation spectroscopy	72
3.5	Pair interactions	76
3.6	Brownian dynamics	82
3.7	Summary	84
	References	85
	Problems	86
4	Electrostatics	88
4.1	Introduction	88
4.2	Electrostatic fields	89
4.3	Boundary conditions	92
4.4	The electric stress tensor	94
4.5	The origins of interfacial charge	96
4.6	The Gouy-Chapman model of the diffuse layer	99
4.7	The diffuse layer near a flat plate	101
4.8	The diffuse layer around a sphere	109
4.9	Repulsion between charged plates	111
4.10	Repulsion between charged spheres	115
4.11	Tests of the Gouy-Chapman theory	120
4.12	Summary	123
	References	124
	Problems	126
5	Dispersion forces	129
5.1	Introduction	129
5.2	Intermolecular forces and the microscopic theory	130
5.3	Overview of the continuum theory	136
5.4	Dielectric response of materials	138
5.5	Theory for flat plates	142
	Solution of the boundary value problem	142
	Interaction potential	145
	Effect of electrolyte	146
5.6	Calculations for specific materials	147
5.7	Geometrical effects: the Derjaguin approximation	149
5.8	Direct measurements	150
5.9	A simplified approximation for flat plates	153
5.10	Interactions between spheres	156
5.11	Summary	158
	References	159
	Problems	160

3

Contents

6	Forces due to soluble polymer	162
6.1	Introduction	163
6.2	Polymers in solution	164
	General features	164
	Thermodynamic functions	168
	Self-consistent field theory	172
	Application to bulk solutions	176
6.3	Terminally anchored polymers	176
	Structure of isolated layers	176
	Interactions between layers: ideal solutions	181
	Interactions between layers: good and poor solvents	183
	Experimental results	186
6.4	Non-adsorbing polymer	189
6.5	Adsorbing polymer	194
	Structure of isolated layers	194
	Interactions between adsorbed layers	201
6.6	Summary	205
	References	206
	Problems	209
7	Electrokinetic phenomena	211
7.1	Introduction	211
	Examples of electrokinetic phenomena	211
	A model problem	212
7.2	Electrophoresis	215
	Scale analysis	216
	A thick diffuse layer	219
	A thin diffuse layer	220
	Electrophoresis with an equilibrium diffuse layer	222
	Effects due to deformation of the diffuse layer	223
	Measurements of electrophoretic mobilities	227
	Comparisons between theory and experiment	229
7.3	Electrical conductivity of dilute suspensions	231
	Maxwell's theory	231
	Diffuse layer effects	232
	Comparisons between theory and experiment	235
7.4	Dilute suspensions with alternating electric fields	238
	The leaky dielectric	239
	Maxwell-Wagner theory	241
	Behavior of suspensions of colloidal particles	243

x Contents

7.5	Summary	252
	References	253
	Problems	256
8	Electrostatic stabilization	258
8.1	Introduction	258
8.2	Inter-particle potential and criteria for stability	260
8.3	Conservation equations for probability densities	262
8.4	Initial stage of Brownian flocculation	267
8.5	Predictions of the stability ratio	271
8.6	Measurements of doublet formation rates	274
8.7	Growth and structure of large flocs	279
8.8	Doublet formation in shear flows	289
	Diffusion dominated flocculation: $Pe \ll 1$	289
	Convection dominated flocculation: $Pe \gg 1$	292
	Growth of large aggregates in shear	298
8.9	Criteria for mechanical stability	299
8.10	Experimental studies of shear flocculation	303
8.11	Summary	305
	References	305
	Problems	308
9	Polymeric stabilization	310
9.1	Introduction	310
9.2	Criteria for stability	312
	Interaction potential between spheres with polymer	
	layers	313
	Stability with respect to dispersion forces	315
	Critical flocculation point	316
9.3	Measurements of critical flocculation point	319
9.4	Summary	327
	References	327
	Problems	328
10	Equilibrium phase behavior	329
10.1	Introduction	329
10.2	The statistical mechanical approach	332
10.3	Equilibrium properties of dilute suspensions	334
10.4	Perturbation theory	335
10.5	Suspensions of hard spheres	338
10.6	Disorder order transition for charged spheres	543

Contents

10.7	Phase transitions induced by dissolved polymer	349
14	Application of the perturbation theory	350
	Hard spheres in ideal polymer solutions	352
	Electrostatically stabilized dispersions	353
	Polymerically stabilized dispersions	357
10.8	Summary	360
	References	361
	Problems	364
		2
11	Particle capture	366
11.1	Introduction	366
	Capture efficiency and the filter coefficient	367
101	Scale analysis	370
11.2	Capture of non-Brownian particles	374
	Inertial capture	375
	Capture with attractive forces	377
	Capture with electrostatic repulsion	380
11.3	Capture of Brownian particles	383
11.4	Experimental measurements	387
	Experiments with rotating discs	388
	Experiments with packed beds	389
11.5	Summary	391
	References	391
	Problems	393
12	Sedimentation	394
12.1	Introduction	394
12.2	Ensemble average velocities	396
12.3	Monodisperse suspensions of spheres	400
12.4	Polydisperse suspensions of spheres	405
12.5	Theory of batch settling	411
12.6	Hard spheres at infinite Peclet number	414
12.7	Hard spheres at finite Peclet number	423
12.8	Summary	425
	References	426
	Problems	427
13	Diffusion	429
13.1	Introduction	429
13.2	Gradient diffusion of monodisperse spheres	432
	1 1	

## xii Contents

13.3	Equilibrium in the presence of an external potential	437
13.4	Principles of photon correlation spectroscopy	441
13.5	Initial decay of the autocorrelation functions	444
13.6	Wavenumber dependent diffusion coefficient	447
13.7	Summary	452
	References	453
	Problems	454
14	Rheology	
14.1	Introduction	456
14.2	Characterization of rheological behavior	457
14.3	Dimensional analysis	464
14.4	Hard spheres	<b>466</b>
14.5	Charged spheres	471
14.6	Polymerically stabilized spheres	477
14.7	Weakly flocculated dispersions	<b>481</b>
1 <b>4.8</b>	Motivation for pair interaction theories	<b>488</b>
14.9	Non-equilibrium microstructure	<b>488</b>
14.10	Macroscopic stresses	493
14.11	Results and comparison with experiment	<b>49</b> 7
14.12	Summary	503
	References	503
	Problems	505
	Appendix A: Measured properties	507
	Appendix B: Vector and tensor notation	508
	Author index	511
	Subject index	517