

# Contents

<i>Preface</i>	v
<b>Chapter 1 Basic Concepts of Colloid Stability</b>	
1.1 General introduction	-
1.2 The nature of colloidal dispersions	2
1.2.1 Particulate dispersions	2
1.2.2 Emulsions and foams	2
1.3 Colloid stability	3
1.3.1 Coagulation and flocculation	3
1.4 The London dispersion attraction	4
1.4.1 The microscopic theory of London attraction	5
1.4.2 The macroscopic theory of London attraction	7
1.5 Strategies for imparting colloid stability	8
1.5.1 Requirements for stabilization	8
1.5.2 Current stabilization methods	8
1.5.2.1 Electrostatic stabilization	8
1.5.2.2 Polymeric stabilization	10
1.5.3 Combinations of stabilization methods	15
1.5.3.1 Electrosteric stabilization	15
1.5.3.2 Other combinations	15
1.5.4 Future stabilization methods	15
1.5.5 Summary of the effects of polymers on colloid stability	16
<b>Chapter 2 Stabilization by Attached Polymer: Steric Stabilization</b>	
2.1 Early technological history	18
2.2 Practical applications	19
2.2.1 Technological applications	19
2.2.2 Biological role	19
2.3 The advantage of steric stabilization	20
2.3.1 Relative insensitivity to the presence of electrolytes	20
2.3.2 Equal efficacy in both aqueous and nonaqueous media	20
2.3.3 Equal efficacy at both high and low solids content	21
2.3.4 Reversibility of flocculation	21

2.4	The early studies of steric stabilization	22
	2.4.1 Aqueous dispersions	22
	2.4.1.1 Biopolymers	22
	2.4.1.2 Synthetic polymers	24
	2.4.2 Nonaqueous dispersions	25
2.5	The misnomer "steric stabilization"	26
2.6	The best steric stabilizers	28
2.7	The preparation of sterically stabilized dispersions	30
<b>Chapter 3</b>	<b>Polymer Solution Thermodynamics</b>	
3.1	Introduction	31
3.2	The Flory-Huggins theory	31
	3.2.1 The combinatorial entropy of mixing	32
	3.2.1.1 The lattice approach	32
	3.2.1.2 The free volume approach to the combinatorial entropy	35
	3.2.2 The enthalpy of mixing	35
	3.2.3 The free energy of mixing	36
	3.2.4 The chemical potentials	37
	3.2.5 The osmotic pressure	38
	3.2.6 The dilution parameters	39
	3.2.7 The theta-point	39
	3.2.7.1 Analogy with the Boyle point	40
	3.2.7.2 Determination of the $\theta$ -point	43
	3.2.8 Failure of the Flory-Huggins theory	46
	3.2.8.1 Concentration dependence of the interaction parameter	46
	3.2.8.2 The entropic component of the interaction parameter	49
	3.2.8.3 Phase separation on heating	50
	3.2.8.4 The defects in the Flory-Huggins theory: an explanation	51
3.3	Flory's equation-of-state theory	53
	3.3.1 Equation-of-state for noninteracting disconnected particles in 1-D	53
	3.3.2 Generalization to 3-D	54
	3.3.3 Inclusion of contact dissimilarity	54
	3.3.4 Incorporation of connectivity	54
	3.3.5 The reduced equation-of-state	55
	3.3.6 Evaluation of the reduced variables	55
	3.3.7 Application to mixtures	56
	3.3.8 Comparison with experiment	56
	3.3.9 Lattice fluid theory	57
3.4	Aqueous polymer solutions	58
<b>Chapter 4</b>	<b>The Conformation of Polymer Molecules</b>	
4.1	Introduction	62
4.2	The dimensions of a polymer chain	62
	4.2.1 The rms end-to-end length	62
	4.2.2 The rms radius of gyration	63
4.3	Models for a polymer chain	64

4.3.1	The random flight chain	64
4.3.1.1	The equivalent freely jointed chain	65
4.3.1.2	The characteristic ratio	66
4.3.1.3	The span and the Hollingsworth radius	67
4.3.2	The freely rotating chain	67
4.3.3	Restrictions to free rotation	68
4.3.3.1	Independent bond rotational potentials	68
4.3.3.2	Interdependent bond rotational potentials	70
4.3.4	The rotational isomeric state theory	71
4.3.5	The unperturbed dimensions	73
4.4	The excluded volume problem	74
4.4.1	The intramolecular expansion factor	74
4.4.2	Theories of excluded volume	74
4.4.2.1	Free chains	74
4.4.2.2	Attached chains	75
4.5	Attached polymer chains	76
4.5.1	The rotational isomeric state method	76
4.5.2	The Gambler's Ruin method	79
4.6	Scaling law theories	79
4.6.1	The basic scaling law	80
4.6.2	The dilute to semi-dilute transition	81
4.6.3	Scaling laws in semi-dilute regime	82
4.6.3.1	The radius of gyration	82
4.6.3.2	The correlation length	84
4.6.3.3	The osmotic pressure	84
4.6.3.4	Summary of some scaling law predictions	85
4.6.3.5	Temperature dependence	85
4.6.3.6	Experimental tests of the scaling law predictions	87
4.6.4	Scaling law theory applied to attached polymer chains	87
4.6.4.1	Segment density profiles	88
4.6.5	Polymers confined to thin slabs	91
<b>Chapter 5</b>	<b>Thermodynamically Limited Steric Stabilization: The Phenomenology of Incipient Flocculation</b>	
5.1	Introduction	92
5.2	General strategy for inducing flocculation	93
5.2.1	The reduction in solvent quality of the dispersion medium	93
5.2.2	The reversibility of flocculation	93
5.2.3	Experimental methods	94
5.2.3.1	The direct turbidity method	94
5.2.3.2	The turbidity-wavelength method	95
5.2.3.3	Rheological methods	96
5.3	The critical flocculation point	97
5.3.1	Designation of various critical flocculation points	98
5.3.2	Influence of system parameters on the critical flocculation point	99
5.3.3	Dependence upon particle concentration	99
5.3.3.1	Experimental	99

## CONTENTS

5.3.4 Dependence of the CFPT on the nature of the anchor polymers	103
5.3.4.1 Aqueous dispersions	104
5.3.4.2 Nonaqueous dispersions	104
5.3.4.3 Conclusion	104
5.3.5 Dependence of the CFPT on particle size	106
5.3.5.1 High molecular weight stabilizing moieties	106
5.3.5.2 Very low molecular weight stabilizing moieties	107
5.3.5.3 Summary	108
5.3.6 Dependence of the CFPT upon surface coverage	108
5.3.6.1 Nonaqueous dispersions	108
5.3.6.2 Aqueous dispersions	109
5.3.6.3 Conclusions	109
5.3.7 Dependence of the CFPT on the nature of the disperse phase	110
5.3.8 Dependence of the CFPT upon molecular weight of the stabilizing moieties	110
5.3.9 The physical nature of flocculation	110
5.3.10 Incipient flocculation overview	112
<b>Chapter 6 Thermodynamically Limited Steric Stabilization: the Identification of the Critical Flocculation Point</b>	
6.1 The correlation between the CFPT and $\theta$ -point	114
6.1.1 The critical flocculation temperatures	115
6.1.2 The critical flocculation pressures	115
6.1.3 The critical flocculation volumes	118
6.1.4 Additional experimental evidence	120
6.1.5 Sterically stabilized emulsions	120
6.1.6 A general rule governing the thermodynamic limit to stability of sterically stabilized systems	121
6.2 Dependence of the CFT upon molecular weight of the stabilizing moieties	121
6.2.1 Dispersions	123
6.2.2 Emulsions	123
6.2.3 Conclusion	124
6.3 The origin of the attraction at the CFT	124
6.3.1 Stabilization by high polymers	124
6.3.1.1 The unimportance of van der Waals forces	124
6.3.1.2 The segmental attraction hypothesis	126
6.3.1.3 Evidence favouring the segmental attraction hypothesis	127
6.3.1.4 Conclusions	127
6.3.2 Stabilization by low molecular weight polymers	127
6.4 The conformation of polymers in worse than $\theta$ -solvents: the coil-globule transition	128
6.4.1 The blob theory	129
6.4.2 Experimental evidence for coil-globule transitions	129
6.4.3 Evidence against coil-globule transitions	130
6.4.4 Reconciliation of the conflicting results	131
6.4.5 Importance for steric stabilization	133

<b>6.5</b>	<b>Other proposals for the identification of the CFPT</b>	<b>133</b>
6.5.1	The phase separation theories	133
6.5.1.1	Experimental test of the phase separation theory	134
6.5.2	The high molecular weight limit postulate	135
6.5.2.1	van der Waals attraction	135
6.5.3	Higher virial coefficients	136
6.5.4	The dipolar substituent theory	137
<b>6.6</b>	<b>Steric stabilization by polyelectrolytes</b>	<b>138</b>
6.6.1	Low degrees of neutralization	138
6.6.2	High degrees of neutralization	139
6.6.3	General discussion	140
<b>6.7</b>	<b>Aqueous dispersions</b>	<b>141</b>
6.7.1	The effects of electrolytes	141
6.7.2	The effects of temperature	143
<b>Chapter 7</b>	<b>Thermodynamically Limited Steric Stabilizations: Thermodynamic Factors Controlling Steric Stabilization</b>	
7.1	The temperature dependence of stability	144
7.2	A general thermodynamic treatment	144
7.3	Identification of the stabilization type by temperature changes	145
7.3.1	Enthalpic stabilization	145
7.3.2	Entropic stabilization	146
7.3.3	Combined enthalpic-entropic stabilization	146
7.4	Identification of the type of stabilization by the dilution parameters	147
7.5	General discussion of the different types of steric stabilization	148
7.5.1	Generality of the classification scheme	148
7.5.2	Typical examples of the classification scheme in action	148
7.5.3	Graphical representation of the domains of steric stabilization	150
7.6	The thermodynamic origins of steric stabilization in the context of the free volume theory	152
7.6.1	Reprise of the free volume theory	152
7.6.1.1	The combinatorial contribution	152
7.6.1.2	The contact of dissimilarity contribution	153
7.6.1.3	The free volume dissimilarity contribution	153
7.6.2	Nonaqueous dispersions	153
7.6.2.1	General considerations	153
7.6.2.2	The effects of temperature changes on stability	156
7.6.3	Aqueous dispersions	157
7.6.3.1	General considerations	157
7.6.3.2	The effects of temperature changes	158
<b>Chapter 8</b>	<b>Non-Thermodynamically Limited Steric Stabilization: Dispersions Displaying Deviant Behaviour</b>	
8.	Introduction	160

8.2	Poorly anchored stabilizing moieties	161
	8.2.1 Copolymers	161
	8.2.2 Steric stabilization by homopolymers	162
8.3	Incomplete surface coverage	162
8.4	Thin steric layers	163
	8.4.1 The effect of particle size	164
	8.4.2 The effect of molecular weight of the stabilizing moieties	165
	8.4.3 The chemical nature of the dispersion medium	166
	8.4.4 The effect of particle number concentration	167
	8.4.5 General discussion of weak coagulation	167
	8.4.5.1 The physical nature of coagulation	167
	8.4.5.2 The temperature induction of weak coagulation	168
	8.4.5.3 The dependence of the CFPT upon the system parameters	169
	8.4.5.4 The critical flocculation particle volume fraction	170
	8.4.6 Comparison of $\theta$ -point flocculation with weak coagulation	177
8.5	Crystallization of the stabilizing moieties	179
<b>Chapter 9</b>	<b>Deviant Flocculation Behaviour: Enhanced Steric Stabilization</b>	
9.1	Introduction	181
9.2	Experimental evidence for enhanced steric stabilization	182
	9.2.1 Homopolymeric stabilizing moieties	182
	9.2.1.1 The importance of surface anchor groups	182
	9.2.1.2 The influence of pH	183
	9.2.1.3 The influence of molecular weight of the stabilizing moieties	184
	9.2.2 Copolymeric stabilizers	185
9.3	The origins of enhanced steric stabilization	187
	9.3.1 The segment reduction hypothesis	188
	9.3.2 Change in thermodynamic parameters	191
	9.3.3 The elastic repulsion hypothesis	191
	9.3.4 Increased mean segment density hypothesis	194
	Conclusions	195
<b>Chapter 10</b>	<b>Stabilization by Attached Polymer: Theories of Steric Stabilization</b>	
10.1	Classification of theories	197
10.2	General considerations of the steric interaction	198
	10.2.1 The three domains of close approach	198
	10.2.1.1 The noninteractional domain	199
	10.2.1.2 The interpenetrational domain	199
	10.2.1.3 The interpenetrational-plus-compressional domain	200
	10.2.2 The components of the steric free energy	200
	10.2.2.1 The mixing free energy	200
	10.2.2.2 The elastic free energy	202

	10.2.3 Interpenetration and flocculation	203
10.3	A general thermodynamic formalism for steric stabilization	204
	10.3.1 The constant segment density model	205
	10.3.1.1 The first virial coefficient term	207
	10.3.1.2 The higher order virial coefficient terms	207
10.4	Models for polymer chains	208
10.5	The early theories of steric stabilization	210
	10.5.1 Loss of configurational entropy theories	210
	10.5.1.1 Mackor	210
	10.5.1.2 Clayfield and Lumb	212
	10.5.1.3 Elastic modulus theory of Jackel	213
<b>Chapter 11</b>	<b>Pseudo-<i>Ab Initio</i> Theories of Steric Stabilization</b>	
11.1	Introduction	216
11.2	The second generation <i>ab initio</i> theories	216
	11.2.1 The germinal theory of Meier for isolated chains	216
	11.2.1.1 The diffusion equation	217
	11.2.1.2 The free energy contributions	217
	11.2.2 Hesselink, Vrij and Overbeek's extension of the Meier theory	222
	11.2.2.1 Total free energy	223
11.3	The potential energy curves for sterically stabilized dispersions	227
	11.3.1 Good solvency conditions	227
	11.3.2 The effect of solvency of the dispersion medium on stability	228
	11.3.3 The effects of molecular weight	230
	11.3.4 The effect of molecular weight polydispersity	230
11.4	Third generation theories	230
	11.4.1 The Edwards approach	230
	11.4.1.1 The self-consistent field theory	231
11.5	Comparison of pseudo- <i>ab initio</i> theories with experiment	239
<b>Chapter 12</b>	<b>The Pragmatic Theories of Steric Stabilization</b>	
12.1	Introduction	241
12.2	The constant segment density theories	242
	12.2.1 The theory of Fischer	242
	12.2.2 Extensions of the Fischer theory	244
12.3	The variable segment density models	245
	12.3.1 Steric barrier layer properties	245
	12.3.1.1 Determination of the segment density distribution functions	246
	12.3.1.2 Arbitrarily chosen segment density functions	251
	12.3.2 Incorporation of a concentration dependent interaction parameter	261
	12.3.2.1 The concentration dependence of the interaction parameter	262
	12.3.2.2 The mixing free energy	263
12.4	The denting hypothesis	267

12.4.1 A statistical mechanical argument against denting	267
12.4.2 Chemical evidence against interpenetration	268
12.4.3 Evidence in favour of interpenetration	269
Predictions of the free volume theory for nonaqueous dispersions	270
12.5.1 The temperature dependence of the interaction parameter	271
12.5.1.1 The macroscopic thermodynamic approach	271
12.5.1.2 The microscopic free volume theory	275
12.5.2 The pressure dependence of the critical flocculation temperature	279
The configurational entropy of colloidal particles	281
12.6.1 The dispersion configurational entropy	281
12.6.2 The configurational free energy change on flocculation	282
<b>Chapter 13 Experimental Studies of the Distance Dependence of Steric Interactions</b>	
13.1 Introduction	283
13.2 Classification of the types of distance dependence studies	283
13.3 Studies of the compression of dispersions	284
13.3.1 2-D compression studies	284
13.3.1.1 The results of Doroszkowski and Lamourne	284
13.3.1.2 The results of Garvey, Mitchell and Smith	287
13.3.2 3-D compression studies	288
13.3.2.1 Osmotic pressure methods	288
13.3.2.2 A filtration method	298
13.4 Interaction of polymer chains attached to macroscopic objects	299
13.4.1 Crossed cylinders	299
13.4.1.1 Experimental apparatus	299
13.4.1.2 Results	301
13.4.2 Crossed filaments	306
13.4.3 Spherical caps	307
13.4.3.1 Apparatus	307
13.4.3.2 Experimental results	309
13.4.4 Thin lipid films	310
13.4.4.1 Oil/water films	310
13.4.4.2 Air/water films	311
13.5 General conclusions	312
<b>Chapter 14 Heterosteric Stabilization and Elastic Stabilization</b>	
14.1 Heterosteric stabilization	314
14.1.1 Introduction	314
14.1.2 Theory	314
14.1.2.1 Parallel flat plates	315
14.1.2.2 Qualitative predictions	317
14.1.2.3 Quantitative predictions	321

14.2	Stabilization in polymer melts	324
14.2.1	Elastic steric stabilization	324
14.2.1.1	Theories of elastic steric stabilization	325
14.2.1.2	Experimental evidence for elastic steric stabilization	326
14.2.2	Heterosteric stabilization in polymer melts	326
14.2.2.1	Theory	326
14.3	Heterosteric stabilization by mixed polymer coatings	329
14.4	The van der Waals interaction	331
<b>Chapter 15</b>	<b>The Effects of Free Polymer on Colloid Stability: Theories of Depletion Flocculation and Depletion Phase Separation</b>	
15.1	Introduction	332
15.2	Depletion flocculation	332
15.2.1	Early theories and experiments	332
15.2.1.1	Theories assuming complete depletion	334
15.2.2	Further developments	338
15.2.2.1	The polymer second virial coefficient	338
15.2.2.2	The particle second virial coefficient	338
15.2.2.3	The partial depletion theories	340
15.2.2.4	The de Gennes theories	340
15.2.2.5	Other theories for flocculation by free polymer	348
<b>Chapter 16</b>	<b>The Effects of Free Polymer on Colloid Stability: Experimental Studies of Depletion Flocculation and Depletion Phase Separation</b>	
16.1	Model experiments on depletion association	353
16.2	The physical nature of the association	353
16.2.1	Phase rule considerations	354
16.2.2	Microgel particles	354
16.2.3	Nonaqueous dispersions	357
16.2.3.1	Phase separation studies	357
16.2.3.2	Flocculation	359
16.2.4	Aqueous dispersions	360
16.2.4.1	Phase separation studies	360
16.2.4.2	Flocculation studies	361
16.3	General discussion of the association phenomena	368
16.3.1	Phase separation	369
16.3.2	Flocculation	371
16.3.2.1	General discussion	371
16.3.2.2	Comparison of experiments with the predictions of the depletion theories	372
<b>Chapter 17</b>	<b>The Effects of Free Polymer on Colloid Stability: Theories of Depletion Stabilization and Depletion Flocculation</b>	
17.1	Introduction	378
17.2	Experimental evidence for depletion stabilization	378
17.2.1	Aqueous systems	378
17.2.1.1	Dependence upon molecular weight and particle radius	379

## CONTENTS

17.3	17.2.2 Nonaqueous dispersions	380
	Qualitative features of depletion stabilization	380
	17.3.1 Résumé of depletion flocculation	380
	17.3.2 Origins of depletion stabilization	380
	17.3.3 Potential energy diagram for depletion stabilization-alone	382
	17.3.4 An alternative approach to depletion stabilization	383
17.4	Quantitative theories of depletion stabilization and depletion flocculation	384
	17.4.1 The theory of Feigin and Napper	385
	17.4.1.1 Segmental density depletion zones	385
	17.4.2 The theory of Scheutjens and Fleer	399
	17.4.3 The theory of Clark and Lal	401
	17.4.4 The nonprediction of depletion stabilization	402
17.5	Thermodynamic formalism for depletion stabilization and depletion flocculation	403
	17.5.1 Conspectus	403
	17.5.2 The effects of gas adsorption on colloid stability	404
	17.5.3 Extension to liquid mixtures	407
	17.5.3.1 Thermodynamic interpretation of depletion flocculation and depletion stabilization	408
17.6	Predictions of the steric layer theory	411
17.7	Summary of the effects of polymers on colloid stability	412
References		414
Subject Index		424