

## Contents

<i>Preface</i>	<i>page</i> xiii
<i>Acknowledgments</i>	xvi
<i>List of symbols</i>	xvii
<b>1 Basic principles and concepts</b>	<b>1</b>
1.1 Introduction	1
1.2 The physics and chemistry of foams and foaming	7
1.3 The wetness and dryness of foams	9
1.4 Capillary pressure and the Laplace–Young equation	11
1.5 Plateau rules and pentagonal dodecahedral structures	12
1.6 Foam structures produced from bubbles with narrow size distributions	16
1.7 Foam structures produced from bubbles with wide size distributions	21
1.8 Surface-active agents are needed to stabilize bubbles and wet foams	23
1.8.1 The adsorption of chemical surfactants at the air/water interface	23
1.8.2 The purity of chemical surfactants in foaming	27
1.8.3 Other types of surface-active materials	28
1.9 Surface tension and surface energy	29
1.10 Gibbs adsorption and Gibbs elasticity	31
1.11 Methods of measuring surface tension	34
1.11.1 Maximum bubble pressure technique	38
1.11.2 Overflow cylinder technique	38
1.11.3 Oscillating jet technique	41
1.12 Foamability and foam stability	41
1.12.1 Surface tension, foamability and foam stability	45
1.12.2 Combining foamability with foam stability	47
1.13 Transition from wet to dry foams	48
<b>2 The nature and properties of foaming surfactants</b>	<b>54</b>
2.1 The formation of self-assemblies from pre-micellar surfactant species	54
2.1.1 Self-association in weakly hydrolysable soaps and fatty acids	56
2.1.2 Solubility and the Krafft point	59

2.2	Geometric packing of surfactant molecules in the interface and the critical packing parameter	60
2.3	Phase behavior of more concentrated surfactant formulations	62
2.4	The influence of the Critical Packing Parameter on foaming	63
2.5	The influence of surfactant solubility on foaming	64
2.6	Anionic surfactants	64
2.7	Nonionic surfactants	65
2.8	Weak hydrolysable fatty acids	66
2.9	Mixed surfactants	68
2.10	The influence of the CMC on foaming	69
2.11	Foaming above the CMC: the influence of the stability of the micellar self-assemblies	71
2.12	Influence of structure on foaming and low-foaming surfactants	75
2.13	The application of the HLB (hydrophile–lipophile) balance concept to foaming	78
2.14	Temperature effects on surface tension and foaming	80
<b>3</b>	<b>Soap bubbles and thin films</b>	<b>84</b>
3.1	Introduction and early studies	84
3.2	20th-century studies on thin liquid films	86
3.3	Experimental techniques for investigating free horizontal circular liquid films	87
3.3.1	The conventional Scheludko/Exerowa thin film balance	87
3.3.2	The porous plug film holder to measure disjoining isotherms and surface forces in thin films	89
3.3.3	The bike wheel microcell film holder	90
3.3.4	The Nikolov/Wasan film balance for measuring drainage and film thickness of curved foam films	91
3.4	Drainage of horizontal thin films	92
3.5	Drainage of vertical thin films	96
3.6	Disjoining pressure isotherms obtained from porous plug experiments	99
3.7	Intermolecular forces are the reason that thin films are stable	99
3.8	The physical chemistry of black films	104
3.9	Rupture mechanism of free microscopic horizontal foam films	105
3.10	Rupture of films between bubbles under dynamic conditions	106
3.11	Importance of fundamental studies on foam films	107
<b>4</b>	<b>Processes in foaming</b>	<b>112</b>
4.1	Overview of processes	112
4.2	Ascent of bubbles in liquids	113
4.2.1	Influence of nonionic surfactants	115
4.2.2	Influence of ionic surfactant	118
4.2.3	Bubbles bouncing from the interface	119

4.2.4	Influence of impact velocity at the interface	120
4.2.5	The detection of surface-active contaminants in water	122
4.3	Drainage of foams	122
4.3.1	Forced, free and pulsed drainage	124
4.3.1.1	Forced drainage	124
4.3.1.2	Free drainage	127
4.3.1.3	Pulsed drainage	127
4.3.2	Influence on interfacial properties	127
4.3.3	Experimental approaches	128
4.3.4	Influence of foam film type	128
4.4	Disproportionation (Ostwald ripening)	130
4.4.1	Experimental methods with foams	132
4.4.2	Experimental methods with thin films	133
4.4.3	Models and theories	134
4.4.3.1	Diffusion theory	135
4.4.3.2	Energy barriers (nucleation theory and fluctuation of holes)	136
4.4.3.3	Freely standing film	137
4.4.3.4	Density fluctuations and accessible area	138
4.4.4	Experimental results	138
4.5	Coupling disproportionation with drainage	144
4.6	Depletion of surfactant from solution	146
4.7	Humidity and evaporation	147
<b>5</b>	<b>Generation of bubbles and foams</b>	<b>155</b>
5.1	Introduction	155
5.2	The adsorption of surfactant on the freshly generated bubbles	155
5.3	Bubble size and distribution	156
5.4	Overview of foam generation techniques	158
5.5	Mechanical methods	159
5.5.1	High-intensity agitation (cavitation)	160
5.5.2	Rotary stirring in food processing	161
5.5.3	Rotary stirring in mineral processing	165
5.5.4	Shaking or successive flipping	168
5.5.5	Pouring and plunging jet methods	170
5.5.5.1	Static plunging jet	170
5.5.5.2	Continuous plunging jet	171
5.6	Growing bubbles from single orifices, frits and gas injection	173
5.6.1	Detachment of a bubble from single orifices	174
5.6.2	Growing bubbles using frits	176
5.6.3	Co-injection	177
5.6.4	Monodispersed bubbles and microfluidic foams	177
5.7	Nucleation of gas bubbles	180

5.7.1	Nucleation of bubbles in champagne and other beverages	181
5.7.2	Dissolved air and column flotation	184
5.8	In situ generation of foams by chemical reactions	186
5.9	Gas generation by electrolysis	188
<b>6</b>	<b>Coalescence of bubbles in surfactant solutions</b>	<b>194</b>
6.1	The formation, break-up and coalescence of bubbles in surfactant solutions	194
6.2	The role of surface tension gradients in coalescence	196
6.3	Relationship between elasticity and critical transition concentration $C_t$	198
6.4	Experimental studies on bubble coalescence	199
6.4.1	Bubble swarm and single bubbles	199
6.4.2	2D Bubble rafts	199
6.4.3	Coalescence at the moment of bubble creation	200
6.4.4	Freely rising single bubble using a laser detector	202
6.4.5	Growing bubbles from adjacent nozzles	205
6.5	Coalescence in aqueous solution of electrolytes	209
6.6	Influence of bubble approach velocity on bubble coalescence	212
6.7	Influence of temperature on coalescence	215
<b>7</b>	<b>The stability/instability of bubbles and foams</b>	<b>220</b>
7.1	Overview	220
7.2	Classification of the stability of foams	222
7.2.1	Unstable (transient) foams	222
7.2.2	Metastable foams	223
7.2.3	High-stability foams	223
7.2.4	Ultrastable foams	223
7.3	Reversing the stability of foams	223
7.3.1	pH-responsive foams	224
7.3.2	Temperature-responsive foams	225
7.3.3	Gas-responsive foams	226
7.4	Gibbs–Marangoni effect	227
7.5	Interfacial rheology	227
7.5.1	Dilational surface viscoelasticity	229
7.5.2	Theories and models	231
7.5.3	Experimental techniques for measurement of elasticity and surface viscosity	232
7.5.4	Oscillating bubble methods	233
7.5.5	Experimental studies of elasticity and surface viscosity	235
7.6	Stability control agents	236
7.6.1	Single surfactant systems, pH, electrolyte and specific ion effects	237

7.6.2	Mixtures of surfactants, foam builders/boosters	238
7.6.3	Polymer/surfactant mixtures	240
7.6.4	Condensed shells	244
7.6.5	Nanopatterning	244
7.6.6	Hydrophobins	244
7.6.7	Control of gas diffusion	246
7.6.7.1	Gas type and foam type	247
7.7	Interfacial rheology and gas permeability	249
7.8	Stability by increase in bulk viscosity	252
7.9	Stability control in aerated food systems	252
7.10	Stratification	253
7.10.1	Hole formation and the diffusion osmotic mechanism	254
7.10.2	Reversible stratification behavior in nonionic surfactants	257
7.10.3	Stratification in charged surfactant systems	258
7.10.4	Stratification in polydispersed systems	259
7.11	Stabilization by liquid crystals	261
7.12	Stabilization by emulsion and pseudo-emulsion films	263
<b>8</b>	<b>Particle-stabilized foams</b>	<b>269</b>
8.1	Introduction	269
8.2	History of particle-stabilized foam systems	271
8.3	Established processes	271
8.4	Fundamentals of collision, contact angles, attachment/detachment	273
8.5	Measurement of attachment time between bubble and particle	275
8.6	Relationship between attachment force and contact angle	275
8.7	Detachment of particles from bubbles	277
8.8	Surface tension of films of attached particles	278
8.9	Interactions between neighboring particles attached to the interface	280
8.10	Key parameters influencing the interactions between bubbles and particles	283
8.11	Steric barriers	284
8.12	Experimental studies relating contact angle and wetting on particle attachment and stability	286
8.13	Janus particles	289
8.14	The influence of concentration, surface charge and state of agglomeration	290
8.15	Simple models of interactions between droplets (bubbles) coated with particles	291
8.16	Models of packing, agglomeration and bridging of particles	293
8.17	Particle/surfactant and particle/polymer mixtures	294
8.17.1	Surface tension measurements of particle/surfactant mixture	296
8.17.2	Gel films	297

8.18	Diffusive disproportionation and shrinkage of particle-laden foams	298
8.19	Drainage with film containing particle/surfactant mixtures	300
8.20	Super particle stabilized foams generated by a magnetic field	302
8.21	Preparation of stabilized monodispersed bubbles with particles	302
<b>9</b>	<b>Foaming in non-aqueous liquids</b>	<b>307</b>
9.1	Introduction	307
9.2	Hydrocarbon-type surfactants	308
9.3	Polymethylsiloxane and fluoroalkyl-type surfactants	309
9.4	Phase separation from partially immiscible liquids	312
9.5	Lamellar liquid crystals, surfactant solid particles and lipid phases	314
9.6	Bulk viscosity	322
9.7	Inorganic electrolytes in non-aqueous liquids	322
9.8	Interfacial charge in non-aqueous systems	324
9.9	Defoaming in non-aqueous solutions	325
9.10	Thin film studies with non-aqueous and ionic liquids	325
<b>10</b>	<b>Antifoaming and defoaming</b>	<b>331</b>
10.1	Background and types of antifoamers and defoamers	331
10.2	Physico-chemical mechanisms	334
10.2.1	Droplets and oil lenses: spreading coefficient ( $S_c$ ), entry coefficient ( $E_c$ ) and bridging coefficient ( $B_c$ )	334
10.2.2	Emulsified droplets and pseudo-emulsion films	338
10.2.3	Effects of disjoining pressure on the stability of the pseudo-emulsion film	338
10.3	Experimental studies	340
10.4	Surface tension gradients, viscosity and drainage	341
10.5	Superspreading	342
10.6	Influence of the interfacial and micellar aggregates	342
10.7	Particles	344
10.8	Cloud-point antifoamer: block copolymers	347
10.9	Fatty alcohol antifoamers: melting point, gel layers and droplet rigidity	347
10.10	Precipitation effects	349
10.11	Mixtures of particles and oils	351
10.12	Fast and slow antifoamers and the film trapping technique	353
10.13	Critical entry pressure for foam film rupture	356
10.14	Influence of the hydrophobicity of solid particles on $E_c$	358
10.15	Influence of the pre-spread oil layer on $E_c$	360
10.16	Ageing effects with chemical antifoamers	360
10.17	Physical methods of defoaming	362
10.17.1	Ultrasonics	363

10.17.2	Suppression of foam by the adjustment of the vessel wettability	367
<b>11</b>	<b>Bubble size measurements and foam test methods</b>	<b>372</b>
11.1	Introduction	372
11.2	Bubble size measurements	374
11.2.1	Direct 2D imaging	374
11.2.2	Optical fiber probe analysis	376
11.2.3	X-ray tomographic imaging	378
11.2.4	Nuclear magnetic resonance imaging and terahertz spectroscopy	380
11.2.5	Ultrasonic imaging	380
11.2.6	Multiple light scattering and back scattering	381
11.3	Bubbly liquids and foam test methods	382
11.3.1	Whipping, shake tests and the Bartsch test method	383
11.3.2	Rotor mixer tests	383
11.3.3	Ross–Miles (pour test)	383
11.3.4	Bikerman test (sparging in a cylindrical column)	385
11.4	Test methods under controlled pressure	388
11.4.1	Time of deviation ( $t_{\text{dev}}$ ) and time of transition ( $t_{\text{tr}}$ )	388
11.4.2	Head space and pressure drop test methods	391
11.5	Electrical conductivity test method (the Foam Scan apparatus)	392
11.6	Measurement of bubbles lifetimes and free microscopic films	394
11.7	Measurement of foam stability in the presence of antifoams/defoamers	397
11.8	Measurement of antifoaming/defoamer performance in washing machines	399
11.9	Comparison of different laboratory foaming test methods	401
<b>12</b>	<b>Bubble and foam chemistry – new areas of foam research</b>	<b>405</b>
12.1	Antibubbles	405
12.2	Foaming research under microgravity	408
12.3	Particle-stabilized foams at high temperatures: metal and material foams	410
12.4	Foams in nature and bio-surfactants	413
	<i>Index</i>	420