CONTENTS

Preface vii

I. INTRODUCTION 1
A. Interfaces 1
B. Colloids 4
C. The bridge to nanoscience 10
1. *What is "nanoscience?"* 10
2. *Nanostructures and assemblies* 12
3. *Generic nanoscience* 17
4. *New tools of generic nanoscience* 18
5. *The plan* 22

II. FLUID INTERFACES AND CAPILLARITY 23
A. Fluid interfaces: Young's membrane model 23
1. *The thinness of interfaces* 23
2. *Definition of surface tension* 25
B. The surface tension of liquids 26
1. *Pure liquids* 26
2. *Temperature dependence of surface tension* 27
3. *Surface tension of solutions* 29
C. Intermolecular forces and the origin of surface tension 31
1. *Van der Waals forces* 31
2. *Surface tension as "unbalanced" intermolecular forces; the Hamaker constant* 35
3. *Pressure deficit in the interfacial layer; Bakker's equation* 37
4. *Components of the surface tension* 41
D. Interfacial tension 43
1. *Experimental interfacial tension* 43
2. *Combining rules for interfacial tension* 43
E. Dynamic surface tension 46
F. Capillary hydrostatics: the Young-Laplace Equation 46
1. *Capillary pressure: pressure jump across a curved fluid interface* 46
2. *The curvature of a surface* 48
3. *Derivation of the Young-Laplace equation* 53
4. *Boundary conditions for the Young-Laplace equation* 55
G. Some solutions to the Young-Laplace equation 57
1. *Cylindrical surfaces; meniscus against a flat plate* 57
2. *Axisymmetric and other surfaces* 59

3. *Nondimensionalization of the Young-Laplace equation; the Bond number* 59
4. *Saddle-shaped surfaces* 62

H. The measurement of surface and interfacial tension 64
1. *Geometric vs. force methods* 64
2. *Capillary rise* 65
3. *Sessile drop and pendant drop* 68
4. *Du Noüy ring detachment* 68
5. *Wilhelmy slide* 69
6. *Langmuir film balance* 70
7. *Drop weight (or volume)* 71
8. *Maximum bubble pressure and dynamic surface tension* 72
9. *The pulsating bubble "surfactometer"* 74
10. *Elliptical (vibrating) jet* 74
11. *Contracting circular jet* 75
12. *Problems with interfacial tension measurement* 75
13. *Spinning drop method* 76

I. Forces on solids in contact with liquids: capillary interactions 76
1. *Liquid bridges* 76
2. *Shared menisci* 80

J. Effect of curvature on the equilibrium properties of bulk liquids: the Kelvin Effect 84
1. *The vapor pressure of small droplets and liquids in pores* 84
2. *The effect of curvature on boiling point* 86
3. *Capillary condensation* 86
4. *Nucleation* 88

K. Thin liquid films 91
1. *Disjoining pressure and its measurement* 91
2. *The molecular origin of disjoining pressure* 94
3. *The disjoining pressure isotherm* 98
4. *The augmented Young-Laplace equation* 101

SOME FUN THINGS TO DO: CHAPTER 2 103

III. THERMODYNAMICS OF INTERFACIAL SYSTEMS 107

A. The thermodynamics of simple bulk systems 107
1. *Thermodynamic concepts* 107
2. *The simple compressible system* 108

B. The simple capillary system 110
1. *The work of extension* 110
2. *Heat effects; abstract properties; definition of boundary tension* 111

C. Extension to fluid-solid interfacial systems 114
1. *The work of area extension in fluid-solid systems* 114
2. *Compound interfacial systems; Young's equation* 116

D. Multicomponent interfacial systems 119
1. *The Gibbs dividing surface and adsorption* 119

2. *Immiscible interfacial systems* 123
3. *The measurement of adsorption* 124
4. *The phase rule; descriptive equations for binary interfacial systems* 127
E. The Gibbs adsorption equation 128
F. Surface tension of solutions 134
1. *Ideal-dilute capillary systems* 134
2. *Moderately dilute capillary systems* 135
G. Surface active agents (surfactants) and their solutions 137
1. *The structure of different types of surface active agents* 137
2. *Solutions of non-electrolyte surfactants* 144
3. *Solutions of electrolyte surfactants* 147
H. Self-assembly of surfactant monomers in solution 148
1. *Formation of micelles: critical micelle concentration (CMC)* 148
2. *Solubilization* 160
I. Micelle morphology, other self-assembled structures, and concentrated surfactant solutions 164
1. *Micellar shape and the Critical Packing Parameter (CPP)* 164
2. *Beyond micelles: other self-assembled structures* 166
3. *Concentrated surfactant solutions; liquid crystalline mesophases* 170
4. *Kinetics of micellization and other self-assembly processes* 171
J. Dynamic surface tension of surfactant solutions 171
1. *Diffusion-controlled adsorption* 171
2. *Finite adsorption-desorption kinetics* 175
K. Insoluble (Langmuir) monolayers 176
1. *Formation of monolayers by spontaneous spreading* 176
2. *Hydrodynamic consequences of monolayers: Gibbs elasticity* 177
3. *π-A isotherms of insoluble monolayers* 178
4. *Langmuir-Blodgett films* 182
5. *Transport properties of monolayers* 184
L. The thermodynamics of fluid-solid interfacial systems revisited 186
1. *The concept of interfacial energy and its measurement in fluid-solid systems* 186
2. *Adsorption of non-polymeric molecules at the solid-liquid interface* 191
3. *Experimental measurement of small molecule solid-liquid adsorption* 201
4. *Adsorption of polymers at the solid-liquid interface* 202
SOME FUN THINGS TO DO: CHAPTER 3 207

IV. SOLID-LIQUID INTERACTIONS 214
A. Wettability and the contact angle: Young's Equation 214
1. *Importance of wetting; definition of contact angle* 214

2. *Young's equation revisited; classification of wetting and contact angle values* 216
B. Contact angle hysteresis 218
1. *Origins of hysteresis: roughness and heterogeneity* 218
2. *Complexity of real surfaces: texture and scale* 221
3. *Wenzel equation for rough surfaces* 223
4. *Cassie-Baxter analysis of heterogeneous surfaces; composite surfaces and ultra-hydrophobicity* 224
5. *The dynamic contact angle; Tanner's law* 227
C. Methods for measuring the contact angle 229
1. *Optical or profile methods: contact angle goniometry* 229
2. *Force methods: contact angle tensiometry* 231
3. *Dynamic contact angle measurement* 235
D. Relation of wetting behavior to surface chemical constitution 236
1. *Zisman plots; the critical surface tension* 236
2. *The wettability series* 238
3. *Estimates of surface energies from contact angle data or vice versa* 239
4. *Thermodynamics of solid-liquid contact: work of adhesion, work of wetting and work of spreading; the Young-Dupré equation* 243
5. *The promotion or retardation of wetting: practical strategies* 245
E. Spreading of liquids on solid surfaces 250
1. *Criteria for spontaneous spreading; spreading morphology* 250
2. *Temperature effects of wetting; heats of immersion and wetting transitions* 254
3. *The kinetics of spreading on smooth surfaces* 255
4. *Spreading agents; superspreaders* 257
F. The relationship of wetting and spreading behavior to adhesion 258
1. *Definition of adhesion; adhesion mechanisms* 258
2. *The "Laws of Molecular Adhesion"* 259
3. *"Practical adhesion" vs. "thermodynamic adhesion"* 261
4. *The importance of wetting (contact angle) to practical adhesion* 263
5. *The optimization of thermodynamic contact adhesion* 264
6. *Acid-base effects in adhesion* 267
7. *Contact mechanics; the JKR method* 272
G. Heterogeneous nucleation 277
H. Processes based on wettability changes or differences 279
1. *Detergency* 279
2. *Flotation* 280
3. *Selective or "spherical" agglomeration* 281
4. *Offset lithographic printing* 282
I. Wicking flows (capillary action) and absorbency 284
1. *Wicking into a single capillary tube* 284

2. *Wicking in porous media* 286
3. *Practical strategies for promoting absorbency* 290
4. *Immiscible displacement* 292
5. *Mercury porosimitry* 292
6. *Motion of liquid threads* 293
7. *Surface wicking; spreading over rough or porous surfaces* 295
J. Particles at interfaces 297
1. *Particles at solid-fluid interfaces: effects on wetting and spreading* 297
2. *The disposition of particles at fluid interfaces* 297
3. *Particle-assisted wetting* 299
4. *Pickering emulsions* 303
5. *Armored bubbles and liquid marbles* 305
6. *Janus particles and nanoparticles at fluid interfaces* 306
K. The description of solid surfaces 309
1. *Solid surface roughness* 309
2. *Fractal surfaces* 310
3. *Surface texture* 313
4. *Measurement of surface roughness and texture by stylus profilometry* 314
L. Optical techniques for surface characterization 315
1. *Optical microscopy* 315
2. *Optical profilometry* 318
3. *Confocal microscopy* 318
4. *Electron microscopy* 319
5. *Near-field scanning optical microscopy (NSOM)* 320
M. Scanning probe microscopy (SPM) 321
1. *Scanning Tunneling Microscopy (STM)* 322
2. *Atomic Force Microscopy (AFM)* 324
N. Surface area of powders, pore size distribution 331
O. Energetic characterization of solid surfaces: Inverse Gas Chromatography (IGC) 333
SOME FUN THINGS TO DO: CHAPTER 4 338

V. COLLOIDAL SYSTEMS: PHENOMENOLOGY AND CHARACTERIZATION 345
A. Preliminaries 345
1. *Definition and classification of colloids* 345
2. *General properties of colloidal dispersions* 346
3. *Dense vs. dilute dispersions* 349
B. Mechanisms of lyophobic colloid instability 351
1. *Phase segregation: the "phoretic processes"* 351
2. *Thermodynamic criteria for stability* 353
3. *Aggregation* 353
4. *Coalescence* 355
5. *Particle size disproportionation* 356

C. Preparation of colloid particles and colloidal dispersions 358
1.*Classification of preparation strategies for lyophobic colloids* 358
2. *Top-down strategies* 360
3. *Bottom-up strategies* 365
D. Morphology of colloids: particle size, size distribution, and particle shape 371
1. *Description of particle size distributions* 371
2. *Distributions based on different size variables and weighting factors* 375
3. *Normal (Gaussian) and log-normal distributions* 379
4. *Particle shape* 382
E. Sedimentation and centrifugation 387
1. *Individual particle settling: Stokes' law* 387
2. *Multi-particle, wall and charge effects on sedimentation* 389
3. *Differential sedimentation; particle size analysis* 391
4. *Centrifugation* 395
F. Brownian motion; sedimentation-diffusion equilibrium 397
1. *Kinetic theory and diffusion* 397
2. *Brownian motion* 399
3. *Sedimentation (centrifugation) – diffusion equilibrium* 403
4. *Practical retrospective regarding sedimentation and other phoretic processes* 407
G. Measurement of particle size and size distribution: overview 409
1. *Classification of methods* 409
2. *Microscopy* 410
H. Light scattering 413
1. *Classical (static) light scattering* 413
2. *Rayleigh scattering* 414
3. *Turbidity* 418
4. *Rayleigh-Gans-Debye (RGD) scattering* 421
5. *Mie scattering* 427
6. *Fraunhofer diffraction; laser diffraction* 429
7. *Inelastic scattering: absorbance; the Raman effect* 431
8. *Scattering from denser dispersions* 436
9. *Dynamic Light Scattering (Photon Correlation Spectroscopy)* 437
10. *Dynamic light scattering from denser dispersions* 442
I. Aperture, chromatographic and acoustic methods for particle sizing 444
1. *Aperture (one-at-a-time) methods* 444
2. *Chromatographic methods* 446
3. *Acoustic methods* 448
SOME FUN THINGS TO DO: CHAPTER 5 450

VI. ELECTRICAL PROPERTIES OF INTERFACES 455
A. Origin of charge separation at interfaces 455
1. *Overview* 455
2. *Preferential adsorption/desorption of lattice ions* 456
3. *Specific adsorption of charged species* 459
4. *Ionization of surface functional groups* 460
5. *Isomorphic substitution* 461
6. *Accumulation/depletion of electrons* 462
7. *Interface charging in non-aqueous systems* 463
B. Electric double layer formation and structure 466
1. *The Helmholtz model; electrostatic units* 466
2. *The Gouy-Chapman model; Poisson-Boltzmann equation* 467
3. *Boundary conditions to the Poisson-Boltzmann equation* 475
4. *Double layers at spherical and cylindrical surfaces* 477
5. *The free energy of double layer formation* 478
6. *The Stern model; structure of the inner part of the double layer* 480
7. *The mercury solution interface; electrocapillarity and refinements to the double layer model* 483
8. *Oriented dipoles at the interface: the χ-potential* 485
C. Electrostatic characterization of colloids by titration methods 487
1. *Colloid titrations* 487
2. *Potentiometric titrations* 488
3. *Conductometric titrations* 492
4. *Donnan equilibrium and the suspension effect* 493
D. Electrokinetics 496
1. *The electrokinetic phenomena* 496
2. *The zeta potential and its interpretation* 500
3. *Electrokinetic measurements; micro-electrophoresis* 503
4. *Relationship of zeta potential to electrophoretic mobility* 508
5. *Electrokinetic titrations* 512
6. *Electro-acoustic measurements* 514
E. Dielectrophoresis and optical trapping 516
1. *Dielectrophoresis* 516
2. *Electrorotation and traveling wave dielectrophoresis* 519
3. *Optical trapping; laser tweezers* 520
SOME FUN THINGS TO DO: CHAPTER 6 523

VII. INTERACTION BETWEEN COLLOID PARTICLES 525
A. Overview and rationale 525
B. Long-range van der Waals interactions 526
1. *The Hamaker (microscopic) approach* 526
2. *Retardation* 530
3. *The Lifshitz (macroscopic) approach* 532
4. *Measurement of Hamaker constants* 535
C. Electrostatic interactions; DLVO theory 540

1. *Electrostatic repulsion between charged flat plates* 540
2. *Electrostatic interactions between curved surfaces; the Derjaguin approximation* 544
3. *DLVO theory: electrocratic dispersions* 547
4. *Jar testing, the Schulze-Hardy rule and agreement with theory* 552
5. *The Hofmeister series; ion speciation and ionic specific adsorption* 554
6. *Repeptization* 556
7. *Interaction between dissimilar surfaces: hetero-aggregation* 558

D. Kinetics of aggregation 560
1. *Classification of aggregation rate processes and nomenclature* 560
2. *Smoluchowski theory of diffusion-limited aggregation* 561
3. *The hydrodynamic drainage effect* 566
4. *Orthokinetic (shear flow induced) aggregation* 568
5. *Reaction-limited (slow) aggregation; the stability ratio W* 569
6. *Secondary minimum effects* 571
7. *Kinetics of hetero-aggregation* 573
8. *Measurement of early-stage aggregation kinetics (W)* 574
9. *Surface aggregation* 577
10. *Electrostatic stabilization and aggregation rates in apolar media* 579

E. Steric stabilization and other colloid-polymer interactions 582
1. *Polymer adsorption and steric stabilization* 582
2. *Thermodynamic considerations: enthalpic vs. entropic effects* 585
3. *Fischer theory* 587
4. *Steric repulsion plotted on DLVO coordinates* 591
5. *Electro-steric stabilization* 595
6. *Bridging flocculation* 596
7. *Depletion flocculation* 597
8. *Electrophoretic displays; electronic paper* 599

F. The kinetics (and thermodynamics) of flocculation 601
G. Other non-DLVO interaction forces 603
H. Aggregate structure evolution; fractal aggregates 607
1. *Stages of the aggregation process* 607
2. *Fractal aggregates* 608
3. *The effect of particle size on aggregation phenomena; coating by nanoparticles* 612

SOME FUN THINGS TO DO: CHAPTER 7 613

VIII. RHEOLOGY OF DISPERSIONS 616
A. Rheology: scope and definitions 616
B. Viscometry 617
1. *Newton's law of viscosity* 617
2. *Measurement of viscosity* 618
C. The viscosity of colloidal dispersions 622
1. *Dilute dispersions; Einstein theory* 622
2. *Denser dispersions of non-interacting particles* 623
3. *Dilute dispersions of non-spherical particles* 625
D. Non-Newtonian rheology 626
1. *General viscous behavior of dispersions of non-interacting particulates* 626
2. *Fluids with a yield stress* 630
3. *Time-dependent rheology* 632
4. *Viscoelasticity* 633
E. Electroviscous effects 637
SOME FUN THINGS TO DO: CHAPTER 8 640

IX. EMULSIONS AND FOAMS 643
A. General consideration of emulsions 643
1. *Classification of emulsions* 643
2. *Emulsifiers and emulsion stability* 644
3. *Thermodynamics of emulsification/breakdown* 649
4. *Preparation of emulsions* 651
B. O/W or W/O emulsions? 652
1. *Rules of thumb* 652
2. *The hydrophile-lipophile balance (HLB) and related scales* 654
3. *Double (or multiple) emulsions* 659
C. Application of emulsions 661
1. *Formation/breaking in situ* 661
2. *Demulsification* 663
D. Microemulsions 664
1. *Distinction between microemulsions and macro emulsions* 664
2. *Phase behavior of microemulsion systems* 666
3. *Ultra-low interfacial tension* 671
4. *Interfacial film properties in microemulsion systems* 672
E. General consideration of foams 673
1. *Nature and preparation of foams* 673
2. *Stages in foam lifetime* 675
3. *Stability mechanisms* 676
4. *Foam behavior and foaming agents* 681
5. *Antifoam action* 684
6. *Froth flotation* 686

7. *Foaming in non-aqueous media; general surface activity near a phase split* 687
SOME FUN THINGS TO DO: CHAPTER 9 691
X. INTERFACIAL HYDRODYNAMICS 695
A. Unbalanced forces at fluid interfaces 695
1. *Unbalanced normal forces* 695
2. *Tangential force imbalances: the Marangoni effect* 696
3. *Boundary conditions at a fluid interface* 702
B. Examples of Interfacial Hydrodynamic Flows 705
1. *The breakup of capillary jets* 705
2. *Steady thermocapillary flow* 712
3. *The motion of bubbles or drops in a temperature gradient* 714
4. *Marangoni instability in a shallow liquid pool–Bénard cells* 718
C. Some Practical Implications of the Marangoni Effect 728
1. *Marangoni effects on mass transfer* 728
2. *Marangoni drying* 732
3. *Marangoni patterning* 733
D. The Effect of Surface Active Agents 735
1. *Gibbs elasticity* 735
2. *The boundary conditions describing the effects of surfactants* 737
3. *The effect of surfactants on bubble or droplet circulation* 740
4. *The effect of surfactants on the stability of a pool heated from below* 745
SOME FUN THINGS TO DO: CHAPTER 10 748
Appendix 1: EXERCISES 753
Appendix 2: THE TOP TEN 767
Appendix 3: OTHER SOURCES 771
Index 773