

CONTENTS

1 NATURE OF COLLOIDAL DISPERSIONS

1.1 Introduction	1
1.2 Technological and biological significance of colloidal dispersions	4
1.3 Classification of colloids	5
1.4 Some typical colloidal dispersions	6
1.5 Brownian motion and diffusion	24
1.6 Electrical charge and colloid stability	33
1.7 Effect of polymers on colloid stability	40

2 THERMODYNAMICS OF SURFACES

2.1 Introduction	45
2.2 Surface energy and its consequences	45
2.3 Thermodynamics of surfaces	56
2.4 The Gibbs adsorption equation	63
2.5 Thermodynamic behaviour of small particles	72
2.6 Equilibrium shape of a crystal	81
2.7 Behaviour of liquids in capillaries	84
2.8 Homogeneous nucleation	93
2.9 Limits of applicability of the Kelvin and Young–Laplace equations	97
2.10 Contact angle and wetting behaviour	100
2.11 Measurement of surface tension and contact angle	112

3 RESPONSE TO EXTERNAL FIELDS AND STRESSES

3.1 Response to gravitational and centrifugal fields	116
3.2 Response of a dielectric material to an electric field	124
3.3 Response to electromagnetic (light) waves	133
3.4 Response to a mechanical stress	144

4 TRANSPORT PROPERTIES OF SUSPENSIONS

4.1 Introduction	157
4.2 The mass conservation equation	158
4.3 Stress in a moving fluid	160
4.4 Stress and velocity field in a fluid in thermodynamic equilibrium	162
4.5 Relationship between the stress tensor and the velocity field	164
4.6 The Navier–Stokes equations	167
4.7 Methods for measuring the viscosity	170
4.8 Sedimentation of a suspension	178
4.9 Brownian motion revisited	181
4.10 The flow properties of suspensions	188

5 PARTICLE SIZE AND SHAPE

5.1 General considerations	201
5.2 Direct microscopic observation	204
5.3 Particle size distribution	213
5.4 Theoretical distribution functions	221
5.5 Sedimentation methods of determining particle size	226
5.6 Electrical pulse counters	232
5.7 Light scattering methods	236
5.8 Hydrodynamic methods	246
5.9 Acoustic methods	250
5.10 Summary of sizing methods	255

6 ADSORPTION ONTO SOLID SURFACES

6.1 Vacuum characterization methods	262
6.2 Some non-vacuum techniques	269
6.3 Adsorption and desorption at the solid–gas interface	277
6.4 Adsorption at the solid–liquid interface	287
6.5 Adsorption of neutral polymers	293

7 ELECTRIFIED INTERFACES: THE ELECTRICAL DOUBLE LAYER

7.1 The electrostatic potential of a phase	305
7.2 The mercury–solution interface	309
7.3 Potential distribution at a flat surface — the Gouy–Chapman model	317
7.4 Comparison with experiment	328
7.5 Adsorption of (uncharged) molecules at the mercury–solution interface	341
7.6 Limitations of the Poisson–Boltzmann equation	342
7.7 The silver iodide–solution interface	344
7.8 Other Nernstian surfaces	355
7.9 Mechanisms of surface charge generation	356
7.10 The double layer on oxide surfaces	361
7.11 The double layer around a sphere	365
7.12 The double layer around a cylinder	369

8 ELECTROKINETICS AND THE ZETA POTENTIAL

8.1 Introduction	374
8.2 Equilibrium double layer theory of electrokinetics	375
8.3 Reciprocity relations	384
8.4 The surface of shear	384
8.5 Measuring electrokinetic properties	387
8.6 Limitations of the elementary theory	393
8.7 The standard double layer model	395
8.8 Double layer dynamics	400
8.9 Electrokinetic effects in thin double layer systems	408
8.10 Numerical solutions of the linearized electrokinetic equations	415
8.11 Electrokinetics in alternating fields	416
8.12 Validity of the electrokinetic equations	426

9 ASSOCIATION COLLOIDS

9.1 The critical micellization concentration (c.m.c.)	435
9.2 Factors affecting the c.m.c.	438
9.3 Equilibrium constant treatment of micelle formation	443
9.4 Thermodynamics of micelle formation	450
9.5 Spectroscopic techniques for investigating micelle structure	460
9.6 Micellar dynamics	466
9.7 Molecular packing and its effect on aggregate formation	472
9.8 Statistical thermodynamics of chain packing in micelles	476

10 ADSORPTION AT CHARGED INTERFACES

10.1 Introduction	482
10.2 Adsorption of potential determining ions	485
10.3 Detection of Stern layer adsorption	490
10.4 The oxide–solution interface	501
10.5 Adsorption of multivalent ions	509
10.6 Surfactant adsorption	518

11 THE THEORY OF VAN DER WAALS FORCES

11.1 Introduction	533
11.2 London theory	536
11.3 Pairwise summation of forces (Hamaker theory)	539
11.4 Retardation effects in Hamaker theory	547
11.5 The Deryaguin approximation	549
11.6 Modern dispersion force theory	552
11.7 Numerical computation of interaction energy	563
11.8 Influence of electrolyte concentration	571
11.9 Theoretical estimation of surface properties	574

12 DOUBLE LAYER INTERACTION AND PARTICLE COAGULATION

12.1 Surface conditions during interaction	582
12.2 Free energy of formation of a double layer	584
12.3 Overlap of two flat double layers	586
12.4 Interaction between dissimilar flat plates	594
12.5 Interaction between two spherical particles	598
12.6 Total potential energy of interaction	601
12.7 Experimental studies of the equilibrium interaction between diffuse double layers	604
12.8 Kinetics of coagulation	616
12.9 Effect of polymers on colloid stability	628

13 INTRODUCTION TO STATISTICAL MECHANICS OF FLUIDS

13.1 Introduction	638
13.2 Molecular interactions	639
13.3 The structure of liquids	641
13.4 The potential of mean force	646

13.5 Time-dependent correlation functions	652
13.6 Applications of the pair distribution function	654
13.7 Measurement of correlation functions	657
13.8 Calculation of distribution functions	663
14 SCATTERING STUDIES OF COLLOID STRUCTURE	
14.1 Introduction	669
14.2 Relating potential to structure	676
14.3 Use of scattering to measure structure	684
14.4 Structure of concentrated isotropic dispersions of spherical particles	698
14.5 Neutron reflectivity	705
15 RHEOLOGY OF COLLOIDAL DISPERSIONS	
15.1 Introduction	714
15.2 Behaviour of time-independent inelastic fluids	715
15.3 Behaviour of time-dependent inelastic fluids	721
15.4 Visco-elastic fluids	724
15.5 Measurement of rheological properties of inelastic fluids in Couette flow	728
15.6 Capillary viscometer	734
15.7 Cone and plate or cone and cone viscometer	739
15.8 Time-dependent inelastic behaviour	740
15.9 Microrheology	741
15.10 Microscopic basis of rheological models	749
APPENDICES	
Appendix A1 Calculation of the allowed surface interaction modes in modern Dispersion Force Theory	767
Appendix A2 Evaluation of the sum of the roots of the dispersion relation	768
Appendix A3 Vector calculus and Poisson's equation	770
Appendix A4 Fourier transforms	777
Appendix A5 Elementary thermodynamic relationships in the absence of surface contributions	780
Appendix A6 Electrical units	784
INDEX	787