

# Contents

|  |           |
|--|-----------|
| <b>Preface</b>   | <b>XI</b> |
| <b>1 Introduction</b>  | <b>1</b>  |
| <b>2 Liquid surfaces</b>   | <b>5</b>  |
| 2.1 Microscopic picture of the liquid surface . . . . .                        | 5         |
| 2.2 Surface tension . . . . .  | 6         |
| 2.3 Equation of Young and Laplace . . . . .                                    | 9         |
| 2.3.1 Curved liquid surfaces . . . . .   | 9         |
| 2.3.2 Derivation of the Young–Laplace equation . . . . .                       | 11        |
| 2.3.3 Applying the Young–Laplace equation . . . . .                            | 12        |
| 2.4 Techniques to measure the surface tension . . . . .                        | 13        |
| 2.5 The Kelvin equation . . . . .  | 16        |
| 2.6 Capillary condensation . . . . .   | 19        |
| 2.7 Nucleation theory . . . . .  | 22        |
| 2.8 Summary . . . . .  | 25        |
| 2.9 Exercises . . . . .  | 26        |
| <b>3 Thermodynamics of interfaces</b>  | <b>29</b> |
| 3.1 The surface excess . . . . .   | 29        |
| 3.2 Fundamental thermodynamic relations . . . . .                              | 32        |
| 3.2.1 Internal energy and Helmholtz energy . . . . .                           | 32        |
| 3.2.2 Equilibrium conditions . . . . .   | 33        |
| 3.2.3 Location of the interface . . . . .                                      | 34        |
| 3.2.4 Gibbs energy and definition of the surface tension . . . . .             | 35        |
| 3.2.5 Helmholtz surface energy, interfacial enthalpy, and Gibbs surface energy | 36        |
| 3.3 The surface tension of pure liquids . . . . .                              | 37        |
| 3.4 Gibbs adsorption isotherm . . . . .  | 39        |
| 3.4.1 Derivation . . . . .   | 39        |
| 3.4.2 System of two components . . . . .                                       | 40        |
| 3.4.3 Experimental aspects . . . . .   | 41        |
| 3.4.4 The Marangoni effect . . . . .   | 42        |
| 3.5 Summary . . . . .  | 43        |
| 3.6 Exercises . . . . .  | 44        |

|          |  |           |
|----------|--|-----------|
| <b>4</b> | <b>The electric double layer</b>                     | <b>45</b> |
| 4.1      | Introduction   | 45        |
| 4.2      | Poisson–Boltzmann theory of the diffuse double layer | 46        |
| 4.2.1    | The Poisson–Boltzmann equation                       | 46        |
| 4.2.2    | Planar surfaces                                      | 47        |
| 4.2.3    | The full one-dimensional case                        | 49        |
| 4.2.4    | The Grahame equation                                 | 52        |
| 4.2.5    | Capacity of the diffuse electric double layer        | 53        |
| 4.3      | Beyond Poisson–Boltzmann theory                      | 54        |
| 4.3.1    | Limitations of the Poisson–Boltzmann theory          | 54        |
| 4.3.2    | The Stern layer                                      | 55        |
| 4.4      | The Gibbs free energy of the electric double layer   | 57        |
| 4.5      | Summary  | 58        |
| 4.6      | Exercises  | 59        |
| <b>5</b> | <b>Effects at charged interfaces</b>                 | <b>61</b> |
| 5.1      | Electrocapillarity                                   | 61        |
| 5.1.1    | Theory   | 62        |
| 5.1.2    | Measurement of electrocapillarity                    | 64        |
| 5.2      | Examples of charged surfaces                         | 65        |
| 5.2.1    | Mercury  | 66        |
| 5.2.2    | Silver iodide  | 67        |
| 5.2.3    | Oxides   | 69        |
| 5.2.4    | Mica   | 70        |
| 5.2.5    | Semiconductors                                       | 71        |
| 5.3      | Measuring surface charge densities                   | 73        |
| 5.3.1    | Potentiometric colloid titration                     | 73        |
| 5.3.2    | Capacitances   | 74        |
| 5.4      | Electrokinetic phenomena: The zeta potential         | 76        |
| 5.4.1    | The Navier–Stokes equation                           | 77        |
| 5.4.2    | Electro-osmosis and streaming potential              | 78        |
| 5.4.3    | Electrophoresis and sedimentation potential          | 80        |
| 5.5      | Types of potentials                                  | 82        |
| 5.6      | Summary  | 84        |
| 5.7      | Exercises  | 84        |
| <b>6</b> | <b>Surface forces</b>                                | <b>85</b> |
| 6.1      | Van der Waals forces between molecules               | 85        |
| 6.2      | The van der Waals force between macroscopic solids   | 89        |
| 6.2.1    | Microscopic approach                                 | 89        |
| 6.2.2    | Macroscopic calculation — Lifshitz theory            | 92        |
| 6.2.3    | Surface energy and Hamaker constant                  | 96        |
| 6.3      | Concepts for the description of surface forces       | 98        |
| 6.3.1    | The Derjaguin approximation                          | 98        |
| 6.3.2    | The disjoining pressure                              | 101       |
| 6.4      | Measurement of surface forces                        | 101       |

|          |  |            |
|----------|--|------------|
| 6.5      | The electrostatic double-layer force . . . . .                     | 103        |
| 6.5.1    | General equations . . . . .  | 103        |
| 6.5.2    | Electrostatic interaction between two identical surfaces . . . . . | 106        |
| 6.5.3    | The DLVO theory . . . . .  | 108        |
| 6.6      | Beyond DLVO theory . . . . .                                       | 110        |
| 6.6.1    | The solvation force and confined liquids . . . . .                 | 110        |
| 6.6.2    | Non DLVO forces in an aqueous medium . . . . .                     | 110        |
| 6.7      | Steric and depletion interaction . . . . .                         | 113        |
| 6.7.1    | Properties of polymers . . . . .                                   | 113        |
| 6.7.2    | Force between polymer coated surfaces . . . . .                    | 114        |
| 6.7.3    | Depletion forces . . . . .   | 116        |
| 6.8      | Spherical particles in contact . . . . .                           | 117        |
| 6.9      | Summary . . . . .  | 121        |
| 6.10     | Exercises . . . . .  | 122        |
| <b>7</b> | <b>Contact angle phenomena and wetting</b>                         | <b>125</b> |
| 7.1      | Young's equation . . . . .   | 125        |
| 7.1.1    | The contact angle . . . . .  | 125        |
| 7.1.2    | Derivation . . . . .   | 126        |
| 7.1.3    | The line tension . . . . .   | 128        |
| 7.1.4    | Complete wetting and wetting transitions . . . . .                 | 128        |
| 7.2      | Important wetting geometries . . . . .                             | 130        |
| 7.2.1    | Capillary rise . . . . .   | 130        |
| 7.2.2    | Particles in the liquid–gas interface . . . . .                    | 131        |
| 7.2.3    | Network of fibers . . . . .  | 132        |
| 7.3      | Measurement of the contact angle . . . . .                         | 133        |
| 7.3.1    | Experimental methods . . . . .                                     | 133        |
| 7.3.2    | Hysteresis in contact angle measurements . . . . .                 | 135        |
| 7.3.3    | Surface roughness and heterogeneity . . . . .                      | 137        |
| 7.4      | Theoretical aspects of contact angle phenomena . . . . .           | 139        |
| 7.5      | Dynamics of wetting and dewetting . . . . .                        | 141        |
| 7.5.1    | Wetting . . . . .  | 141        |
| 7.5.2    | Dewetting . . . . .  | 145        |
| 7.6      | Applications . . . . .   | 146        |
| 7.6.1    | Flotation . . . . .  | 146        |
| 7.6.2    | Detergency . . . . .   | 147        |
| 7.6.3    | Microfluidics . . . . .  | 148        |
| 7.6.4    | Adjustable wetting . . . . .                                       | 150        |
| 7.7      | Summary . . . . .  | 151        |
| 7.8      | Exercises . . . . .  | 152        |
| <b>8</b> | <b>Solid surfaces</b>  | <b>153</b> |
| 8.1      | Introduction . . . . .   | 153        |
| 8.2      | Description of crystalline surfaces . . . . .                      | 154        |
| 8.2.1    | The substrate structure . . . . .                                  | 154        |

|          |  |            |
|----------|--|------------|
| 8.2.2    | Surface relaxation and reconstruction . . . . .                          | 155        |
| 8.2.3    | Description of adsorbate structures . . . . .                            | 158        |
| 8.3      | Preparation of clean surfaces . . . . .                                  | 158        |
| 8.4      | Thermodynamics of solid surfaces . . . . .                               | 161        |
| 8.4.1    | Surface stress and surface tension . . . . .                             | 161        |
| 8.4.2    | Determination of the surface energy . . . . .                            | 164        |
| 8.4.3    | Surface steps and defects . . . . .                                      | 167        |
| 8.5      | Solid–solid interfaces . . . . .   | 169        |
| 8.6      | Microscopy of solid surfaces . . . . .                                   | 171        |
| 8.6.1    | Optical microscopy . . . . .   | 171        |
| 8.6.2    | Electron microscopy . . . . .  | 172        |
| 8.6.3    | Scanning probe microscopy . . . . .                                      | 174        |
| 8.7      | Diffraction methods . . . . .  | 177        |
| 8.7.1    | Diffraction patterns of two-dimensional periodic structures . . . . .    | 177        |
| 8.7.2    | Diffraction with electrons, X-rays, and atoms . . . . .                  | 179        |
| 8.8      | Spectroscopic methods . . . . .  | 181        |
| 8.8.1    | Spectroscopy using mainly inner electrons . . . . .                      | 181        |
| 8.8.2    | Spectroscopy with outer electrons . . . . .                              | 182        |
| 8.8.3    | Secondary ion mass spectrometry . . . . .                                | 183        |
| 8.9      | Summary . . . . .  | 185        |
| 8.10     | Exercises . . . . .  | 185        |
| <b>9</b> | <b>Adsorption</b> . . . . .  | <b>187</b> |
| 9.1      | Introduction . . . . .   | 187        |
| 9.1.1    | Definitions . . . . .  | 187        |
| 9.1.2    | The adsorption time . . . . .  | 188        |
| 9.1.3    | Classification of adsorption isotherms . . . . .                         | 189        |
| 9.1.4    | Presentation of adsorption isotherms . . . . .                           | 191        |
| 9.2      | Thermodynamics of adsorption . . . . .                                   | 192        |
| 9.2.1    | Heats of adsorption . . . . .  | 192        |
| 9.2.2    | Differential quantities of adsorption and experimental results . . . . . | 193        |
| 9.3      | Adsorption models . . . . .  | 195        |
| 9.3.1    | The Langmuir adsorption isotherm . . . . .                               | 195        |
| 9.3.2    | The Langmuir constant and the Gibbs energy of adsorption . . . . .       | 198        |
| 9.3.3    | Langmuir adsorption with lateral interactions . . . . .                  | 199        |
| 9.3.4    | The BET adsorption isotherm . . . . .                                    | 199        |
| 9.3.5    | Adsorption on heterogeneous surfaces . . . . .                           | 202        |
| 9.3.6    | The potential theory of Polanyi . . . . .                                | 203        |
| 9.4      | Experimental aspects of adsorption from the gas phase . . . . .          | 206        |
| 9.4.1    | Measurement of adsorption isotherms . . . . .                            | 206        |
| 9.4.2    | Procedures to measure the specific surface area . . . . .                | 209        |
| 9.4.3    | Adsorption on porous solids — hysteresis . . . . .                       | 211        |
| 9.4.4    | Special aspects of chemisorption . . . . .                               | 214        |
| 9.5      | Adsorption from solution . . . . .                                       | 215        |
| 9.6      | Summary . . . . .  | 217        |
| 9.7      | Exercises . . . . .  | 217        |

|   |            |
|---|------------|
| <b>10 Surface modification</b>                        | <b>219</b> |
| 10.1 Introduction                                     | 219        |
| 10.2 Chemical vapor deposition                        | 220        |
| 10.3 Soft matter deposition                           | 222        |
| 10.3.1 Self-assembled monolayers                      | 222        |
| 10.3.2 Physisorption of Polymers                      | 226        |
| 10.3.3 Polymerization on surfaces                     | 228        |
| 10.3.4 Plasma polymerization                          | 230        |
| 10.4 Etching techniques                               | 232        |
| 10.5 Lithography                                      | 235        |
| 10.6 Summary  | 237        |
| 10.7 Exercises  | 238        |
| <b>11 Friction, lubrication, and wear</b>             | <b>241</b> |
| 11.1 Friction   | 241        |
| 11.1.1 Introduction                                   | 241        |
| 11.1.2 Amontons' and Coulomb's Law                    | 242        |
| 11.1.3 Static, kinetic, and stick-slip friction       | 244        |
| 11.1.4 Rolling friction                               | 245        |
| 11.1.5 Friction and adhesion                          | 247        |
| 11.1.6 Experimental Aspects                           | 247        |
| 11.1.7 Techniques to measure friction                 | 247        |
| 11.1.8 Macroscopic friction                           | 249        |
| 11.1.9 Microscopic friction                           | 250        |
| 11.2 Lubrication                                      | 253        |
| 11.2.1 Hydrodynamic lubrication                       | 254        |
| 11.2.2 Boundary lubrication                           | 256        |
| 11.2.3 Thin film lubrication                          | 257        |
| 11.2.4 Lubricants                                     | 258        |
| 11.3 Wear   | 259        |
| 11.4 Summary  | 261        |
| 11.5 Exercises  | 262        |
| <b>12 Surfactants, micelles, emulsions, and foams</b> | <b>265</b> |
| 12.1 Surfactants                                      | 265        |
| 12.2 Spherical micelles, cylinders, and bilayers      | 269        |
| 12.2.1 The critical micelle concentration             | 269        |
| 12.2.2 Influence of temperature                       | 271        |
| 12.2.3 Thermodynamics of micellization                | 272        |
| 12.2.4 Structure of surfactant aggregates             | 274        |
| 12.2.5 Biological membranes                           | 277        |
| 12.3 Macroemulsions                                   | 278        |
| 12.3.1 General properties                             | 278        |
| 12.3.2 Formation                                      | 280        |
| 12.3.3 Stabilization                                  | 282        |

|                 |   |            |
|-----------------|---|------------|
| 12.3.4          | Evolution and aging . . . . .                                 | 285        |
| 12.3.5          | Coalescence and demulsification . . . . .                     | 287        |
| 12.4            | Microemulsions . . . . .                                      | 287        |
| 12.4.1          | Size of droplets . . . . .                                    | 288        |
| 12.4.2          | Elastic properties of surfactant films . . . . .              | 289        |
| 12.4.3          | Factors influencing the structure of microemulsions . . . . . | 290        |
| 12.5            | Foams . . . . .   | 292        |
| 12.5.1          | Classification, application and formation . . . . .           | 292        |
| 12.5.2          | Structure of foams . . . . .                                  | 293        |
| 12.5.3          | Soap films . . . . .  | 294        |
| 12.5.4          | Evolution of foams . . . . .                                  | 297        |
| 12.6            | Summary . . . . .   | 298        |
| 12.7            | Exercises . . . . .   | 298        |
| <b>13</b>       | <b>Thin films on surfaces of liquids</b>                      | <b>301</b> |
| 13.1            | Introduction . . . . .  | 301        |
| 13.2            | Phases of monomolecular films . . . . .                       | 304        |
| 13.3            | Experimental techniques to study monolayers . . . . .         | 307        |
| 13.3.1          | Optical methods . . . . .                                     | 307        |
| 13.3.2          | X-ray reflection and diffraction . . . . .                    | 308        |
| 13.3.3          | The surface potential . . . . .                               | 311        |
| 13.3.4          | Surface elasticity and viscosity . . . . .                    | 313        |
| 13.4            | Langmuir–Blodgett transfer . . . . .                          | 314        |
| 13.5            | Thick films – spreading of one liquid on another . . . . .    | 316        |
| 13.6            | Summary . . . . .   | 318        |
| 13.7            | Exercises . . . . .   | 319        |
| <b>14</b>       | <b>Solutions to exercises</b>                                 | <b>321</b> |
| <b>Appendix</b> |   |            |
| <b>A</b>        | <b>Analysis of diffraction patterns</b>                       | <b>343</b> |
| A.1             | Diffraction at three dimensional crystals . . . . .           | 343        |
| A.1.1           | Bragg condition . . . . .                                     | 343        |
| A.1.2           | Laue condition . . . . .                                      | 344        |
| A.1.3           | The reciprocal lattice . . . . .                              | 345        |
| A.1.4           | Ewald construction . . . . .                                  | 347        |
| A.2             | Diffraction at Surfaces . . . . .                             | 347        |
| A.3             | Intensity of diffraction peaks . . . . .                      | 349        |
| <b>B</b>        | <b>Symbols and abbreviations</b>                              | <b>353</b> |
|                 | <b>Bibliography</b>   | <b>357</b> |
|                 | <b>Index</b>  | <b>379</b> |