CONTENTS

Chapter 1. FORCES NEAR INTERFACES 1

Introduction 1

1.1. Molecular and Electric Forces in Interfacial Layers 4

1.2. Formation and Structure of Electrical Double Layers 8

1.3. Diffuse Part of the EDL. The Poisson–Boltzmann Equation 9

1.4. The Debye–Hückel Equation. Relation between Surface Potential and Surface Charge 12

1.5. Planar Double Layer. Some Exact Solutions of the General Poisson–Boltzmann Equation . 13

1.6. More Complex Situations: Curved Surface, and Discreteness of Surface Charge 15

1.7. Adsorption of Ions in the Stern Layer . . . 16

1.8. Charging of Surfaces by Dissociation of Ionogenic Groups 18

1.9. Testing of Models of Ionized Surfaces . . . 18

References 19

Chapter 2. DISJOINING PRESSURE 25

2.1. Two Kinds of Surface Force 25

2.2. Definition of Disjoining Pressure 27

2.3. Relationship between Disjoining Pressure and Other Thermodynamic Functions 31

2.4. Pressure Distribution in the Interfacial Transition Zone 33

2.5. Refinement of the Definition of Disjoining Pressure 36

2.6. Equilibrium of Films under Gravity 40

2.7. Hydrodynamics of Thin Films 44

2.8. Thermodynamic Theory of Interaction between Bodies with Curved Surfaces 46

References 51

Chapter 3. THE THERMODYNAMIC THEORY OF STABILITY OF THIN FILMS 53

3.1. Stability and Equilibrium of Interlayers between Parallel Plates 53

3.2. Stability of Interlayers between Convex Bodies 55

3.3. Stability of Wetting Films 57

3.4. Stability of Interlayers between Two Identical Fluids 59

References 83

Chapter 4. DISPERSION FORCES IN THIN INTERLAYERS AND FILMS 85

4.1. Historical Background of the Theory of Intermolecular Forces 85

4.2. Direct Measurements of Molecular Attraction between Two Solids 88

4.3. Experimental Results 93

4.4. The Theory of Molecular Attraction between Macroscopic Objects 98

4.4.1. Calculation of the Interaction between Macroscopic Objects by Summing the Interactions between Microobjects 98

4.4.2. E. M. Lifshitz's Macroscopic Theory of Molecular Attraction between Condensed-State Bodies 100

4.5. Comparison of the Results of Early Experiments with the Theory 106

4.5.1. Comparison with the Results of Calculations Carried Out by the Method of Summation of All Pairwise Molecular Interactions 106

4.5.2. Comparison with the Macroscopic Theory of Molecular Attraction . . . 106

4.6. Current Status of the Macroscopic Theory of Molecular Forces 109

4.7. Main Results of the Experimental Verification of the Theory of Molecular Interaction between Macroscopic Bodies 128

References 146

Chapter 5. THE ADSORPTION COMPONENT OF DISJOINING PRESSURE IN NONIONIC SOLUTIONS 151

References 171

Chapter 6. THE ELECTROSTATIC COMPONENT OF DISJOINING PRESSURE 173

6.1. Methods of Calculation of Disjoining Pressure Π_e 173

6.2. Interaction between Identical Layers. Boundary Conditions 179

6.3. Interaction at Constant Charge or at Constant Surface Potential 181

6.4. Interaction between Double Layers in Asymmetrical Electrolytes 183

6.5. Some Approximate Formulas for Disjoining Pressure 185

6.6. Gibbs Free Energy of the Interaction between Flat Double Layers under Different Boundary Conditions 189

6.7. Interaction between Charged Spherical Particles 193

6.8. Interaction between Unequally Charged Surfaces 198

6.9. Effect of Discreteness of Surface Charge . . 210

6.10. Disjoining Pressure in a Thin Free Film . . 218

6.11. Experimental Verification of the Theory of Electrostatic Interaction 222

References 228

Chapter 7. THE STRUCTURE OF BOUNDARY LAYERS OF LIQUIDS AND THE STRUCTURAL COMPONENT OF DISJOINING PRESSURE 231

7.1. Structural Changes in Thin Interlayers and Boundary Layers of Water 232

7.2. Boundary Layers with Liquid-Crystal Structure 244

7.3. Boundary Layers of Nonpolar Liquids 252

7.4. The Study of Boundary Layers of Liquids by the Blow-Off Technique 253

7.5. Theory of the Structural Component of Disjoining Pressure 264

7.6. Experimental Isotherms of the Structural Component of Disjoining Pressure 271

References 283

Chapter 8. THE DERJAGUIN–LANDAU–VERWEY–OVERBEEK (DLVO) THEORY OF STABILITY OF LYOPHOBIC COLLOIDS . 293

8.1. Effects of Electrolytes on Lyophobic Colloids 293

8.2. Kinetics of Coagulation of Lyophobic Colloids 296

8.3. Coagulation Criteria 297

8.4. Exact Solution 300

8.5. Effect of Charging Mechanism 302

8.6. Further Development and Verification of the DLVO Theory 305

References 308

Chapter 9. THE THEORY OF HETEROCOAGULATION IN LYOPHOBIC SYSTEMS 311

9.1. Destabilization Criteria for Heterodispersions with a Positive Hamaker Constant . . . 312

9.2. Destabilization Criteria for Dispersions with a Negative Hamaker Constant 319

9.3. Development and Verification of the Theory . 323

References 325

Chapter 10. WETTING FILMS 327

10.1. Disjoining Pressure of Wetting Films 327

10.2. Experimental Methods of Determining the Disjoining Pressure Isotherms of Wetting Films. 330

10.3. Disjoining Pressure Isotherms of Wetting Films Formed by Various Liquids 338

10.4. Wetting Films on Nonflat Surfaces 359

References 364

Chapter 11. SURFACE FORCES IN TRANSPORT PHENOMENA . . . 369

11.1. Capillary Osmosis 369

11.2. Reverse Osmosis 380

11.3. Diffusiophoresis 388

11.4. Thermo-osmosis, the Mechanocaloric Effect, and Thermophoresis 390

11.5. Thermocrystallization Flow in Thin Non-freezing interlayers 409

References 427

Conclusion 433

Index 435