## Contents

Preface to the Third Edition  xvi
Preface to the Second Edition  xix
Preface to the First Edition  xx

**PART ONE  THE FORCES BETWEEN ATOMS AND MOLECULES**  

1. Historical Perspective  3
   1.1. The Four Forces of Nature  3
   1.2. Greek and Medieval Notions of Intermolecular Forces  3
   1.3. The Seventeenth Century: First Scientific Period  5
   1.4. The Eighteenth Century: Confusion, Contradictions, and Controversy  7
   1.5. The Nineteenth Century: Continuum *versus* Molecular Theories  8
   1.6. Intermolecular Force-Laws and Interaction Potentials: Long- and Short-Range Forces  9
   1.7. First Successful Phenomenological Theories  12
   1.8. First Estimates of Molecular Sizes  15
   1.9. The Twentieth Century: Understanding Simple Systems  16
   1.10. Recent Trends  17

*Problems and Discussion Topics*  18

2. Thermodynamic and Statistical Aspects of Intermolecular Forces  23
   2.1. The Interaction of Molecules in Free Space and in a Medium  23
   2.2. Self-Energy and Pair Potential  25
   2.3. The Boltzmann Distribution and the Chemical Potential  26
4.2. Dipole Self-Energy 73
4.3. Ion-Dipole Interactions 73
4.4. Ions in Polar Solvents 78
4.5. Strong Ion-Dipole Interactions in Water: Hydrated Ions 78
4.6. Solvation Forces, Structural Forces, and Hydration Forces 80
4.7. Dipole-Dipole Interactions 81
4.8. Magnetic Dipoles 83
4.9. Hydrogen Bonds 83
4.10. Rotating Dipoles and Angle-Averaged Potentials 84
4.11. Entropic Effects 86

Problems and Discussion Topics 88

5. Interactions Involving the Polarization of Molecules 91
5.1. The Polarizability of Atoms and Molecules 91
5.2. The Polarizability of Polar Molecules 93
5.3. Other Polarization Mechanisms and the Effects of Polarization on Electrostatic Interactions 94
5.4. Interactions between Ions and Uncharged Molecules 96
5.5. Ion-Solvent Molecule Interactions and the Born Energy 98
5.6. Dipole-Induced Dipole Interactions 99
5.7. Unification of Polarization Interactions 99
5.8. Solvent Effects and “Excess Polarizabilities” 100

Problems and Discussion Topics 105

6. Van der Waals Forces 107
6.2. Strength of Dispersion Forces: Van der Waals Solids and Liquids 109
6.3. Van der Waals Equation of State 113
6.4. Gas-Liquid and Liquid-Solid Phase Transitions in 3D and 2D 115
6.5. Van der Waals Forces between Polar Molecules 117
6.6. General Theory of Van der Waals Forces between Molecules 119
6.7. Van der Waals Forces in a Medium 122
6.8. Dispersion Self-Energy of a Molecule in a Medium 126
6.9. Further Aspects of Van der Waals Forces: Anisotropy (Orientation), Nonadditivity (Many-Body), and Retardation Effects 127

Problems and Discussion Topics 130

7. Repulsive Steric Forces, Total Intermolecular Pair Potentials, and Liquid Structure 133
7.1. Sizes of Atoms, Molecules, and Ions 133
7.2. Repulsive Potentials 136
7.3. Total Intermolecular Pair Potentials: Their Form, Magnitude, and Range 136
7.4. Role of Repulsive Forces in Noncovalently Bonded Solids 140
7.5. Packing of Molecules and Particles in Solids 142
7.6. Role of Repulsive Forces in Liquids: Liquid Structure 145
7.7. The Effect of Liquid Structure on Molecular Forces 147

Problems and Discussion Topics 148

8. Special Interactions: Hydrogen-Bonding and Hydrophobic and Hydrophilic Interactions 151
8.1. The Unique Properties of Water 151
8.2. The Hydrogen Bond 152
8.3. Models of Water and Associated Liquids 156
8.4. Relative Strengths of Different Types of Interactions 157
8.5. The Hydrophobic Effect 158
8.6. The Hydrophobic Interaction 161
8.7. Hydrophilic Interactions 163

Problems and Discussion Topics 166

9. Nonequilibrium and Time-Dependent Interactions 169
9.1. Time- and Rate-Dependent Interactions and Processes 169
9.2. Rate- and Time-Depended Detachment (Debonding) Forces 171
9.3. Energy Transfer (Dissipation) during Molecular Collisions: the Deborah Number 175
9.4. Energy Transfer during Cyclic Bonding-Unbonding Processes 178
9.5. Relationships between Time, Temperature, and Velocity (Rate) in Complex Processes 182

Problems and Discussion Topics 185

PART TWO THE FORCES BETWEEN PARTICLES AND SURFACES 189

10. Unifying Concepts in Intermolecular and Interparticle Forces 191

10.1. The Association of Like Molecules or Particles in a Medium 191
10.2. Two Like Surfaces Coming Together in a Medium: Surface and Interfacial Energy 196
10.3. The Association of Unlike Molecules, Particles, or Surfaces in a Third Medium 197
10.4. Particle-Surface and Particle-Interface Interactions 198
10.5. Engulfing and Ejection 200
10.6. Adsorbed Surface Films: Wetting and Nonwetting 201

Problems and Discussion Topics 203

11. Contrasts between Intermolecular, Interparticle, and Intersurface Forces 205

11.1. Short-Range and Long-Range Effects of a Force: Qualitative Differences in the Interactions of Particles and Small Molecules 205
11.2. Interaction Potentials between Macroscopic Bodies 208
11.3. Effective Interaction Area of Two Spheres: the Langbein Approximation 211
11.4. Interactions of Particles Compared to Those between Atoms or Small Molecules 212
13.8. Applications of the Lifshitz Theory to Interactions in a Medium 264
13.9. Repulsive Van der Waals Forces: Disjoining Pressure and Wetting Films 267
13.10. Van der Waals Forces at Large Separations: Retardation Effects 270
13.11. Electrostatic Screening Effects in Electrolyte Solutions 274
13.12. Combining Relations 274
13.13. Surface and Adhesion Energies 275
13.15. Forces between Surfaces with Adsorbed Layers 281
13.16. Experiments on Van der Waals Forces 282

Problems and Discussion Topics 284

14. Electrostatic Forces between Surfaces in Liquids 291
14.2. Charged Surfaces in Water: No Added Electrolyte—“Counterions Only” 293
14.3. The Poisson-Boltzmann (PB) Equation 293
14.4. Surface Charge, Electric Field, and Counterion Concentration at a Surface: “Contact” Values 294
14.5. Counterion Concentration Profile Away from a Surface 296
14.7. The Pressure between Two Charged Surfaces in Water: the Contact Value Theorem 300
14.8. Limit of Large Separations: Thick Wetting Films 303
14.9. Limit of Small Separations: Osmotic Limit and Charge Regulation 305
14.10. Charged Surfaces in Electrolyte Solutions 306
14.11. The Grahame Equation 308
14.12. Surface Charge and Potential of Isolated Surfaces 309
14.13. Effect of Divalent Ions 311
14.14. The Debye Length 312
14.15. Variation of Potential $\psi_x$ and Ionic Concentrations $\rho_x$ Away from a Surface 313
14.16. Electrostatic Double-Layer Interaction Forces and Energies between Various Particle Surfaces 314
14.17. Exact Solutions for Constant Charge and Constant Potential Interactions: Charge Regulation 318
14.18. Asymmetric Surfaces 321
14.19. Ion-Condensation and Ion-Correlation Forces 322
14.21. Van der Waals and Double-Layer Forces Acting Together: the DLVO Theory 326
14.22. Experimental Measurements of Double-Layer and DLVO Forces 331
14.23. Electrokinetic Forces 334
14.24. Discrete Surface Charges and Dipoles 335

Problems and Discussion Topics 338

15. Solvation, Structural, and Hydration Forces 341
15.1. Non-DLVO Forces 341
15.2. Molecular Ordering at Surfaces, Interfaces, and in Thin Films 342
15.3. Ordering of Spherical Molecules between Two Smooth (Unstructured) Surfaces 345
15.4. Ordering of Nonspherical Molecules between Structured Surfaces 347
15.5. Origin of Main Type of Solvation Force: the Oscillatory Force 349
15.6. Jamming 354
15.7. Experimental Measurements and Properties of Oscillatory Forces 355
15.8. Solvation Forces in Aqueous Systems: Monotonically Repulsive “Hydration” Forces 361
15.9. Solvation Forces in Aqueous Systems: Attractive "Hydrophobic" Forces 370

Problems and Discussion Topics 378

16. Steric (Polymer-Mediated) and Thermal Fluctuation Forces 381
16.1. Diffuse Interfaces in Liquids 381
16.2. The States of Polymers in Solution and at Surfaces 381
16.3. Repulsive "Steric" or "Overlap" Forces between Polymer-Covered Surfaces 387
16.4. Interparticle Forces in Pure Polymer Liquids (Polymer Melts) 393
16.5. Attractive "Intersegment" and "Bridging" Forces 394
16.6. Attractive "Depletion" Forces 398
16.7. Polyelectrolytes 402
16.8. Nonequilibrium Aspects of Polymer Interactions 404
16.9. Thermal Fluctuations of and Forces between Fluid-Like Interfaces 405
16.10. Short-Range Protrusion Forces 406
16.11. Long-Range Undulation Forces 408

Problems and Discussion Topics 411

17. Adhesion and Wetting Phenomena 415
17.1. Surface and Interfacial Energies 415
17.2. Adhesion Energies versus Adhesion Forces 419
17.3. Highly Curved Surfaces and Interfaces: Clusters, Cavities, and Nanoparticles 422
17.4. Contact Angles and Wetting Films 429
17.5. Wetting of Rough, Textured, and Chemically Heterogeneous Surfaces 434
17.6. Contact Angle Hysteresis 439
17.7. Adhesion of Solid Particles: the JKR and Hertz Theories 442
17.8. Adhesion Hysteresis 448
17.9. Adhesion of Rough and Textured Surfaces 452
17.10. Plastic Deformations 453
17.11. Capillary Forces 456

Problems and Discussion Topics 461

18. Friction and Lubrication Forces 469
18.1. Origin of Friction and Lubrication Forces 469
18.2. Relationship between Adhesion and Friction Forces 476
18.3. Amontons' Laws of (Dry) Friction 481
18.4. Smooth and Stick-Slip Sliding 482
18.5. Lubricated Sliding 485
18.6. Transitions between Liquid- and Solid-Like Films 490
18.7. The "Real" Area of Contact of Rough Surfaces 493
18.8. Rolling Friction 494
18.9. Theoretical Modeling of Friction Mechanisms 495

Problems and Discussion Topics 497

PART THREE SELF-ASSEMBLING STRUCTURES AND BIOLOGICAL SYSTEMS 501

19. Thermodynamic Principles of Self-Assembly 503
19.1. Introduction: Soft Structures 503
19.2. Fundamental Thermodynamic Equations of Self-Assembly 504
19.3. Conditions Necessary for the Formation of Aggregates 509
19.4. Effect of Dimensionality and Geometry: Rods, Discs, and Spheres 510
19.5. The Critical Micelle Concentration (CMC) 512
19.6. Infinite Aggregates (Phase Separation) versus Finite Sized Aggregates (Micellization) 513
19.7. Hydrophobic Energy of Transfer 514
19.8. Nucleation and Growth of Aggregates 515
19.9. 2D Structures on Surfaces: Soluble and Insoluble Monolayers 520
19.10. Line Tension and 2D Micelles (Domains) 521
19.11. Soluble Monolayers and the Gibbs Adsorption Isotherm 524
19.12. Size Distributions of Self-Assembled Structures 524
19.13. Large and More Complex Amphiphilic Structures 527

Problems and Discussion Topics 530

20. Soft and Biological Structures 535

20.1. Introduction: Equilibrium Considerations of Fluid Amphiphilic Structures 535
20.2. Optimal Headgroup Area 536
20.3. Geometric Packing Considerations 538
20.4. Spherical Micelles 540
20.5. Nonspherical and Cylindrical Micelles 543
20.6. Bilayers 544
20.7. Vesicles 548
20.8. Curvature/Bending Energies and Elasticities of Monolayers and Bilayers 550
20.9. Other Amphiphilic Structures and the Transitions between Them 558
20.10. Self-Assembly on Surfaces and Interfaces: 2D Micelles, Domains, and Rafts 562
20.11. Biological Membranes 564
20.12. Membrane Lipids 564
20.13. Membrane Proteins and Membrane Structure 567

Problems and Discussion Topics 569

21. Interactions of Biological Membranes and Structures 577

21.1. Van der Waals Forces 577
21.2. Electrostatic (Double-Layer) and DLVO Forces 579