## Contents

26

Pref	face to t	the Third Edition xvii	
Pref	face to t	the Second Edition xix	
Pref	face to t	the First Edition xxi	
DA	DT ON	IF THE FORCES DETINIEEN ATOMS AND	
PA	KI ON	NE THE FORCES BETWEEN ATOMS AND MOLECULES	1
	1. Histo	orical 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 <i>versus</i> 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
	Prob	lems and Discussion Topics	18
		modynamic and Statistical Aspects termolecular Forces	23
	2.1.	The Interaction of Molecules in Free Space and in a Medium	23
	2.2.	Self-Energy and Pair Potential	25

The Boltzmann Distribution and the Chemical Potential

2.3.

	2.4.	The Distribution of Molecules and Particles in Systems at Equilibrium	27
	2.5.	The Van der Waals Equation of State (EOS)	30
	2.6.	The Criterion of the Thermal Energy $kT$ for Gauging the Strength of an Interaction	31
	2.7.	Classification of Forces and Pair Potentials	34
	2.8.	Theoretical Analyses of Multimolecular Systems: Continuum and Molecular Approaches	35
	2.9.	Molecular Approaches via Computer Simulations: Monte Carlo (MC) and Molecular Dynamics (MD)	37
	2.10.	Newton's Laws Applied to Two-Body Collisions	39
	2.11.	Kinetic and Statistical Aspects of Multiple Collisions: the Boltzmann Distribution	43
	Probl	lems and Discussion Topics	49
3.		ng Intermolecular Forces: Covalent Coulomb Interactions	53
	3.1.	Covalent or Chemical Bonding Forces	53
	3.2.	Physical and Chemical Bonds	54
	3.3.	Coulomb Forces or Charge-Charge Interactions, Gauss's Law	55
	3.4.	Ionic Crystals	58
	3.5.	Reference States	59
	3.6.	Range of Electrostatic Forces	60
	3.7.	The Born Energy of an Ion	61
	3.8.	Solubility of Ions in Different Solvents	62
	3.9.	Specific Ion-Solvent Effects: Continuum Approach	66
	3.10.	Molecular Approach: Computer Simulations and Integral Equations of Many-Body Systems	67
	Probi	lems and Discussion Topics	68
4.	Inter	actions Involving Polar Molecules	71
	4.1.	What Are Polar Molecules?	71

	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
	6.1. Origin of the Van der Waals-dispersion Force between Neutral Molecules: the London Equation	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-Dependent 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

F

	11.5.	Interaction Energies and Interaction Forces: the Derjaguin Approximation	215
	11.6.	"Body Forces" and "Surface Forces"	220
	Probl	lems and Discussion Topics	220
12.	Force	e-Measuring Techniques	223
	12.1.	Direct and Indirect Measurements of Intermolecular, Interparticle, and Surface Forces	223
	12.2.	Different Direct Force-Measuring Techniques	227
	12.3.	Mechanics of Direct Force Measurements and Problems of Interpretation	231
	12.4.	Measuring Force-Distance Functions, $F(D)$	234
	12.5.	Instabilities	235
	12.6.	Measuring Adhesion Forces and Energies	237
	12.7.	Measuring Forces between Macroscopic Surfaces: the SFA, OP/OS and Related Techniques	239
	12.8.	Measuring Forces between Microscopic (Colloidal) and Nanoscopic Particles: AFM and TIRM Techniques	245
	12.9.	Measuring Single-Molecule and Single-Bond Interactions: OT and MC Techniques	248
	Probl	lems and Discussion Topics	250
13.	Van	der Waals Forces between Particles and Surfaces	253
	13.1.	Van der Waals Force-Laws for Bodies of Different Geometries: the Hamaker Constant	253
	13.2.	Strength of Van der Waals Forces between Bodies in a Vacuum or Air	254
	13.3.	The Lifshitz Theory of Van der Waals Forces	256
	13.4.	Particle-Surface Interactions	259
	13.5.	Nonretarded Hamaker Constants Calculated on the Basis of the Lifshitz Theory	260
	13.6.	Van der Waals Forces between Conducting Media	261
	13.7.	Theoretical and Experimental Hamaker Constants for Interactions in a Vacuum or Air	263

	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
	13.14.	Surface Energies of Metals	280
	13.15.	Forces between Surfaces with Adsorbed Layers	281
	13.16.	Experiments on Van der Waals Forces	282
	Proble	ms and Discussion Topics	284
4.	Electro	ostatic Forces between Surfaces in Liquids	291
	14.1.	The Charging of Surfaces in Liquids: the Electric "Double-Layer"	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
	14.6.	Origin of the Ionic Distribution, Electric Field, Surface Potential, and Pressure	298
	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 $\psi_{\rm x}$ and Ionic Concentrations $\rho_{\rm x}$ 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
	14.20. More Complex Systems: Finite Reservoir Systems and Finite Ion-Size Effects	325
	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
5.	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

		Solvation Forces in Aqueous Systems: Attractive "Hydrophobic" Forces	370
	Proble	ms 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
	Proble	ems and Discussion Topics	411
17.	Adhes	sion 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
	Proble	ems and Discussion Topics	461
18.	Frictio	on 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
	Proble	ems and Discussion Topics	497
AR	THE	REE SELF-ASSEMBLING STRUCTURES	
		AND BIOLOGICAL SYSTEMS	501
19.	Thern	nodynamic 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,	F10
	10.5	Discs, and Spheres  The Critical Micelle Concentration (CMC)	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
	<ul><li>19.7.</li><li>19.8.</li></ul>	Hydrophobic Energy of Transfer Nucleation and Growth of Aggregates	514 515

P

	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
	19.14. Effects of Interactions between Aggregates: Mesophases and Multilayers	528
	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

	21.3.	Repulsive Entropic (Thermal Fluctuation, Steric-Hydration) Forces: Protrusion, Headgroup Overlap, and Undulation Forces	585
	21.4.	Attractive Depletion Forces	593
	21.5.	Attractive Hydrophobic Forces	595
	21.6.	Biospecificity: Complementary, Site-Specific and Ligand-Receptor (LR) Interactions	599
	21.7.	Bridging (Tethering) Forces	603
	21.8.	Interdependence of Intermembrane and Intramembrane Forces	605
	21.9.	Biomembrane Adhesion, Bioadhesion	607
	21.10.	. Membrane Fusion	611
	Probl	ems and Discussion Topics	613
22.	Dyna	mic Biointeractions	617
	22.1.	Subtleties of Biological Forces and Interactions	617
	22.2.	Interactions that Evolve in Space and Time: Some General Considerations	617
	22.3.	Biological Rupture and Capture: the Bell and Jarzynski Equations	619
	22.4.	Multiple Bonds in Series and in Parallel	622
	22.5.	Detachment versus Capture Processes: Biological Importance of "Rare Events"	626
	22.6.	Dynamic Interactions between Biological Membranes and Biosurfaces	626
	22.7.	Self-Assembly versus Directed Assembly: Dynamic Phases and Tunable Materials	628
	22.8.	Motor Proteins, Transport Proteins, and Protein Engines	630
	Probl	ems and Discussion Topics	631
Refere	nces	635	

Index 663