

# Contents

## 1. The Chemistry and Physics of Solid Adhesion

*Lieng-Huang Lee*

1. Introduction	1
2. The Four Forces of Nature	2
2.1. Carriers of Four Forces	3
2.2. Gluons and Adhesion of Nuclei	4
2.3. Nuclear Equation of State	5
3. Chemical Bonding and Intermolecular Forces	6
3.1. Chemical Forces and Covalent Bonding	6
3.2. Coulomb Force and Ionic Bond	6
3.3. Electronegativity and Partial Ionic Bond	7
3.4. Lifshitz–van der Waals Forces Between Microscopic Bodies	8
3.5. Nonretarded Lifshitz–van der Waals Forces Between Macroscopic Bodies	11
4. Molecular Interactions	16
4.1. Morse Interaction Curve	16
4.2. Perturbation Theory	17
4.3. Kitaura–Morokuma’s Decomposition of Interaction Energies	18
4.4. Natural Bond Orbital (NBO) Donor–Acceptor Approach	19
4.5. Acid–Base Interaction	21
5. Role of Diffusion in Adhesion	23
5.1. Fick’s Laws of Diffusion	23
5.2. Activation Energy of Diffusion	24
5.3. Diffusion and Adhesion of Polymers	24
5.4. Diffusion of Solid into Polymers	26
6. Physicochemical Bonding on Solid Surfaces	26
6.1. Density of States (DOS)	26
6.2. Electron Work Function	27
6.3. Fermi Energy	28
6.4. Frontier Orbital Concept	30
7. Interactions on Solid Surfaces	32
7.1. Interactions Between Two Discrete Molecules	32

7.2.	Interactions Between a Molecule and a Solid	32
7.3.	Chemisorption	33
8.	Hard-Soft Acid-Base (HSAB) Principle	33
8.1.	The HSAB Principle in Solution	33
8.2.	Extension of the HSAB Principle to the Solid State	34
9.	Metal-to-Metal Contact	35
9.1.	Metal-Metal Adhesion	36
9.2.	Metal-Metal Adhesion Theory	36
9.3.	Effect of Critical Separation on Metal-Metal Adhesion	36
9.4.	Effect of the Acid-Base Interaction on Metal-Metal Adhesion	37
9.5.	Effect of Crystal Structure on Metal-Metal Adhesion	37
9.6.	Effect of Contact Electrification on Metal-Metal Adhesion	38
9.7.	Effect of Diffusion on Metal-Metal Adhesion	38
10.	Metal-Semiconductor Contact	39
10.1.	Ionicity of Semiconductors	40
10.2.	Metal-Semiconductor Adhesion	41
10.3.	Effect of Chemical Reaction on Metal-Semiconductor Interface	41
10.4.	Effect of Contact Electrification on Metal-Semiconductor Adhesion	42
11.	Metal-Salt and Metal-Oxide Adhesion	45
12.	Metal-Ceramic Adhesion	46
13.	Metal-Superconductor Adhesion	48
14.	Metal-Glass Adhesion	48
15.	Metal-Diamond Adhesion	49
16.	Metal-Polymer Adhesion	50
16.1.	Mechanisms of Metal-Polymer Adhesion	50
16.2.	Classification of Polymers According to their Wettabilities	50
16.3.	Metal Adhesion to Low Wettability Polymers	51
16.4.	Metal Adhesion of Medium Wettability Polymers	55
16.5.	Metal Adhesion to High Wettability Polymers	56
16.6.	Metal-Rubber Adhesion	60
16.7.	Effect of Contact Electrification on Metal-Polymer Adhesion	62
17.	Polymer-Solid Adhesion	63
17.1.	Polymer-Solid Contact	64
17.2.	Polymers as Adhesives	66
18.	Discussion	67
19.	Summary	71
Appendix		72
A.	Fundamental Physical Constants	72
B.	Non-SI Units Used with SI	72
Acknowledgment		72

Nomenclature .....	73
References .....	75

## 2. Thermodynamics of Adhesion

*W. Gutowski*

1. Molecular Forces .....	87
1.1. General .....	87
1.2. Types of Intermolecular and Interatomic Forces, Their Range and Magnitude .....	87
1.3. Classical (Microscopic) Theory of Interatomic and Intermolecular Forces .....	89
1.4. Application of Quantum Field Theory for Estimation of Interaction Force and Energy Between Two Solids (Macroscopic Theory) .....	98
2. Acid–Base (Donor–Acceptor) Interactions .....	105
2.1. Brønsted and Lewis Concepts of Acid–Base Interactions .....	105
2.2. Acidity and Basicity of Solid Surfaces .....	106
2.3. Quantitative Assessment of Acid–Base Interactions .....	109
2.4. Acid–Base Interactions in Adhesion .....	113
3. Thermodynamics of Surfaces .....	116
3.1. Surface Energy, Thermodynamic Work of Adhesion, and Energy of Cohesion .....	116
3.2. Energy Equilibrium at the Interface .....	117
3.3. Interfacial Energy .....	118
4. Experimental Techniques .....	123
4.1. Interfacial Energy at the Liquid–Liquid and Liquid–Gas Interface by Techniques Independent of Contact Angle .....	124
4.2. Techniques Based on Measurement of the Equilibrium Contact Angle .....	124
4.3. Techniques Based on Acid–Base Interaction Concepts .....	131
Nomenclature .....	132
References .....	133

## 3. Theory of Adhesive Forces Across Interfaces: 1. The Lifshitz–van der Waals Component of Interaction and Adhesion

*Robert J. Good and Manoj K. Chaudhury*

1. Introduction .....	137
2. Theory of van der Waals Interactions Across Interfaces .....	137
2.1. The Pairwise-Addition Approximation .....	137
2.2. The Lifshitz Theory: General Considerations .....	140

3. Interactions Between Condensed Phases .....	142
4. Application to Interfacial Tension and Free Energy .....	145
Appendix. A Note on Electrostatic and Electromagnetic Units in the Theory of Adhesion .....	147
Nomenclature .....	149
References .....	150
<b>4. Theory of Adhesive Forces Across Interfaces: 2. Interfacial Hydrogen Bonds as Acid–Base Phenomena and as Factors Enhancing Adhesion</b>	
<i>Robert J. Good, Manoj K. Chaudhury, and Carel J. van Oss</i>	
1. Introduction .....	153
2. Monopolar and Bipolar Substances and Hydrogen Bonds <i>per se</i> ...	154
3. Classification of Binary Systems .....	157
4. Surface Parameters $\gamma^{\oplus}$ and $\gamma^{\ominus}$ That Give Direct Characterization of Acidic and Basic Behavior .....	160
5. Application of the Lewis Acid–Base Parameters .....	162
5.1. $\gamma^{\oplus}$ and $\gamma^{\ominus}$ Values of Selected Liquids .....	163
5.2. Application to Selected Solid Surfaces .....	164
5.3. Discussion of $\gamma^{\oplus}$ and $\gamma^{\ominus}$ Values in Table 5 .....	165
6. An Anomaly .....	167
7. Applications .....	167
7.1. Negative Interfacial Tensions: An Illustration .....	167
7.2. Application to Adhesion and Adhesive Bonding .....	168
7.3. The Effective Range of Acid–Base Interactions .....	169
7.4. Other Developments and Applications .....	169
8. Summary .....	170
Nomenclature .....	170
References .....	171
<b>5. The Dynamics of Wetting</b>	
<i>P. G. de Gennes</i>	
1. Introduction .....	173
2. The Final State in Complete Wetting .....	174
3. The Dynamics of Dry Spreading .....	175
4. Special Systems .....	177
4.1. Polymer Melts .....	177
4.2. Langmuir–Blodgett Deposition .....	177
5. Conclusions .....	178
Acknowledgments .....	178
Nomenclature .....	178
References .....	179

## 6. Kinetics of Polymer–Polymer Interdiffusion

### *F. Brochard-Wyart*

1. Introduction	181
1.1. Interdiffusion Coefficient	181
1.2. Interdiffusion Profiles	186
2. Dynamics of Pure Melts—Autoadhesion	188
2.1. Polymer Melts: Statics and Dynamics	189
2.2. Reptation and Self-Diffusion of Entangled Polymers	190
2.3. Interdiffusion of Labeled $P_A^*$ /Unlabeled $P_A$ Polymers	191
2.4. Autoadhesion: Polymer–Polymer Welding	193
3. Dynamics of $P_A/P_B$ Mixtures: Heterojunctions	196
3.1. The Flory–Huggins Free Energy of Mixing	196
3.2. Microscopic Theory of Mutual Diffusion	197
3.3. Interdiffusion of Small Chains ( $N_A, N_B < N_e$ )	199
3.4. Interdiffusion of Entangled Polymers ( $N_A, N_B > N_e$ )	201
3.5. $P_A/P_B$ Welding (Short-Time Behavior)	202
4. Conclusions	202
Acknowledgments	203
Nomenclature	204
References	204

## 7. Welding, Tack, and Green Strength of Polymers

### *Richard P. Wool*

1. Introduction	207
2. Theory	208
2.1. Molecular Dynamics of Random-Coil Chains	208
2.2. Molecular Description of a Polymer–Polymer Interface	209
2.3. Concentration Profile	214
2.4. Scaling Laws for a Polymer–Polymer Interface	215
3. Fractal Nature of a Diffusion Front	216
3.1. Atomic Diffusion Front	216
3.2. Computer Analysis of Polymer–Polymer Interdiffusion	218
4. Microstructural Fracture Criteria	220
4.1. Chain Pullout	220
4.2. Fracture Mechanics of Welding	222
4.3. Stages of Healing	227
5. Healing Experiments	229
5.1. Tack and Green Strength	229
6. Welding of Polymer Interfaces	233
6.1. Wedge Cleavage Experiment	233
7. Lap Shear Welding	241
7.1. Polystyrene Welding	241

8. Polymer Processing Weld Lines .....	242
8.1. Compression Molding .....	242
Acknowledgments .....	244
Nomenclature .....	244
References .....	246

## 8. Role of Electrostatics in Adhesion

*Dan A. Hays*

1. Introduction .....	249
2. Electrostatic Concepts .....	251
3. Electrostatic Force Between a Point Charge and Planar Material ...	253
4. Electrostatic Force Between Charged Planar Materials .....	254
5. Charge Exchange Properties of Materials .....	258
5.1. Metal–Metal Charging .....	259
5.2. Metal–Insulator Charging .....	261
5.3. Insulator–Insulator Charging .....	265
6. Charge Penetration Depth in Insulators .....	266
7. Charge Back-Flow During Separation .....	268
8. Interfacial Polarization .....	269
9. Charged Particle Adhesion .....	270
10. Summary .....	275
Nomenclature .....	275
References .....	276

## 9. Adhesion Through Silane Coupling Agents

*Edwin P. Plueddemann*

1. Introduction .....	279
2. General Equilibrium Conditions .....	280
2.1. Reaction with the Mineral .....	281
2.2. Hydrophobic Interphase Region .....	281
2.3. Optimum Structure in the Interphase Region .....	282
3. Crosslinking the Interphase Region .....	285
3.1. Inhibition of Cure by Fillers .....	285
3.2. Inhibition of Cure by Silanes .....	286
3.3. Additional Crosslinking Through the Coupling Agent .....	286
3.4. Additional Crosslinking Through Siliconates .....	287
4. Conclusion .....	289
References .....	289

## 10. Adhesive–Adherend Interface and Interphase

*James D. Miller and Hatsuo Ishida*

1. Introduction .....	291
2. Interface .....	292

3. Chemical Modifiers .....	297
4. Evidence of Chemical Bonding .....	302
5. Interphase .....	308
5.1. Theories .....	308
5.2. Properties .....	310
5.3. Silane Interphase .....	314
5.4. Other Additives .....	318
6. Future Directions .....	319
References .....	320

## 11. Adhesion at Metal Interfaces

*Amitava Banerjea, John Ferrante, and John R. Smith*

1. Introduction .....	325
2. Theoretical Considerations .....	327
2.1. First-Principle Calculations .....	328
2.2. Jellium-Model Calculations .....	329
3. Binding Energies .....	333
3.1. Fully Three-Dimensional Calculations .....	335
3.2. Universality in the Shapes of the Binding Energy Curves .....	337
4. Semiempirical Techniques .....	338
4.1. Embedded-Atom Method .....	338
4.2. Equivalent-Crystal Theory .....	339
5. Concluding Remarks .....	345
Nomenclature .....	346
References .....	347

## 12. Hard-Soft Acid-Base (HSAB) Principle for Solid Adhesion and Surface Interactions

*Lieng-Huang Lee*

1. Introduction .....	349
2. HSAB Principle .....	349
2.1. HSAB Principle for Inorganic Reactions .....	349
2.2. HSAB Principle for Organic Reactions and the Frontier Orbital Approach .....	350
2.3. Perturbation Equation .....	350
2.4. Electronegativity and Absolute Hardness .....	351
3. Extension of the HSAB Principle to Solid Interactions .....	353
3.1. Electronic Band Structures of Solids .....	353
3.2. Average Energy Gap and Absolute Hardness .....	354
3.3. Energy Gaps and Absolute Hardness Values for Semiconductors .....	354
3.4. Absolute Hardness of Solid .....	357

4. Applications of the HSAB Principle to Adhesion and Surface Interactions Between Metals and Polymers .....	358
5. Conclusions .....	359
Acknowledgments .....	359
Nomenclature .....	360
References .....	360

### 13. Interface Design for Thin Film Adhesion

*John E. E. Baglin*

1. Introduction .....	363
2. Origins of Thin Film Adhesion .....	364
2.1. Interface Energy .....	364
2.2. Interface Fracture .....	365
3. Adhesion Performance .....	366
3.1. Dependence on Application .....	366
3.2. Adhesion Measurements .....	367
4. Adhesion Enhancement .....	370
4.1. Processing Strategies .....	370
4.2. Ion Beam Techniques .....	371
5. Summary .....	381
References .....	381

### 14. Chemistry, Microstructure, and Adhesion of Metal-Polymer Interfaces

*Paul S. Ho, Richard Haight, Robert C. White, B. D. Silverman, and F. Faupel*

1. Introduction .....	383
2. Chemical Bonding and Electronic Structure .....	385
2.1. Electronic Structure of Polyimide Surface .....	385
2.2. Chromium-Polyimide Interface .....	388
2.3. Copper-Polyimide Interface .....	391
3. Interfacial Microstructure .....	393
4. Adhesion and Deformation .....	399
5. Summary .....	404
Acknowledgments .....	405
References .....	405

### 15. Aspects of Bioadhesion

*Robert E. Baier and Anne E. Meyer*

1. Introduction .....	407
2. Analytical Methods Most Applicable to Bioadhesion Studies .....	409



3. Experimental Requirements .....	410
4. Bioadhesion of Microbes .....	410
5. Bioadhesion of Macrobiota .....	415
6. Bioadhesion from Blood .....	415
7. Bioadhesion in Hard and Soft Tissues .....	417
8. Research Priorities for Future Bioadhesion Studies .....	419
9. Summary and Conclusions .....	420
10. Postscript: Universality of the Principle of Bioabhesion .....	421
Acknowledgments .....	422
References .....	422
<b>About the Contributors .....</b>	<b>427</b>
<b>Author Index .....</b>	<b>431</b>
<b>Subject Index .....</b>	<b>437</b>