# FUNDAMENTALS OF INTERFACIAL ENGINEERING

ROBERT J. STOKES D. FENNELL EVANS



## **CONTENTS**

Fundamental Constants xxviii

Conversions and Useful Relations xxviiii

1	1	Defining	<b>Interfacial</b>	Engineering	1
---	---	----------	--------------------	-------------	---

- 1.1 What Is Interfacial Engineering? 1
- 1.2 Trends in Interfacial Products and Processes 1
  - 1.2.1 Computer Chips and Packaging 1
  - 1,2.2 Photographic Films 3
  - 1.2.3 Polymer Composites 3
  - 1.2.4 Advanced Ceramics 4
  - 1.2.5 Breadth of Field 5
- 1.3 Reproducibility and Reliability 5
- 1.4 Organization and Goals of This Book 6
  - 1.4.1 Interfacial Phenomena in Fluids and Solids Are Treated Separately 6
  - 1.4.2 Interfacial Engineering Embodies Both Macroscopic and Microscopic Levels of Understanding 7
  - 1.4.3 Subject Headings and Concept Maps Provide Different Levels of Overview of the Subject Matter 8

## 2 / Interaction Forces in Interfacial Systems 9

- 2.1 Interaction Forces between Molecules Can Be Most Simply Described as a Sum of Five Contributions 14
- 2.2 Interactions between Permanently Charged Molecules and Polar Molecules—Coulomb's Law Describes Attractive and Repulsive Interactions 17
  - 2.2.1 Depending on the Sign of the Charges, Ion—Ion Interactions Can Be Attractive or Repulsive 17
  - 2.2.2 Ion-Dipole Interactions Depend on the Orientation of the Ion and the Dipole 18
  - 2.2.3 Dipole-Dipole Interaction Energies Are Often Less Than Thermal Energy 20
  - 2.2.4 When Electrostatic Interactions Are
    Comparable to the Thermal Energy, We
    Use Angle-Averaged Interaction Potentials
    to Evaluate the Interaction Energy 22
  - 2.2.5 When Angle-Averaged Interaction Potentials
    Are Computed for Dipole-Dipole

interactions, We Obtain th	e Keeson
Attractive Interaction Ener	gv <i>23</i>

- 2.2.6 The Interaction Energy for Angle-Averaged
  Potentials Is Twice the Interaction Free
  Energy 24
- 2.3 Interactions between Permanently Charged
  Molecules or Polar Molecules and Induced
  Dipoles—Attractive Interactions Occur When
  Electrical Fields Emanating from a Polar Molecule
  Induce Polarization in Nearby Molecules 24
  - 2.3.1 Induced Dipole Interactions Exhibit Only Half the Energy of Direct Interactions 24
  - 2.3.2 Comparing Ion-Induced Dipole Interactions with Ion-Dipole Interactions Shows That Induced Interactions Are More Short-Ranged 27
  - 2.3.3 When Angle-Averaged Potentials Are Computed for Dipole-Induced Dipole Interactions, We Obtain the Debye Attractive Interaction 27
- 2.4 Interactions between Induced Dipoles and Induced Dipoles—Dispersion Forces—Lead to Attractive Interactions between All Molecules 28
- 2.5 We Can Obtain the van der Waals Attractive Force by Combining Expressions for the Keesom, Debye, and London Forces 29
  - 2.5.1 Potential Energy Curves Describing
    Intermolecular Interactions in the Vapor
    Phase Combine Expressions for van der
    Waals Attractions and Hard Sphere
    Repulsions 29
  - 2.5.2 Dispersion Forces Determine the Properties of van der Waals Solids Composed of Inert, Spherical Molecules 32
- 2.6 We Can Express Interaction Forces between Particles by a Sum of Terms Similar to That Used to Express the Interaction between Molecules 34
  - 2.6.1 We Can Obtain the Dispersion Forces
    Acting between Two Particles or
    Macroscopic Bodies in Vacuum by
    Summing the London Dispersion Forces
    over All Molecules Contained in the Two
    Bodies on a Pairwise Basis 34
  - 2.6.2 Interaction Forces between Spheres Can Be Obtained from the Interaction Energy between Parallel Plates 36
  - 2,6.3 Attractive Energies between Particles Are Much Smaller in a Condensed Phase Than in Vacuum 39
- 2.7 The Boltzmann Equation Provides the Basis for Deciding When Interfacial Energies Are Important 41

## 3 / General Properties of Systems Containing Fluid Interfaces 45

- 3.1 Surface Tension Is the Key Concept in Characterizing Fluid Interfaces 52
  - 3.1.1 Molecular Origins of Surface and Interface
    Tension Can Be Understood in Terms of
    Differences in Interaction between
    Molecules in the Bulk and at the
    Interface 53
- 3.2 The Relation between Surface Tension and Work of Cohesion and Adhesion Affects the Spontaneous Spreading of One Liquid upon Another 57
  - 3.2.1 Work of Cohesion and of Adhesion Are Key Concepts in Understanding Many Interfacial Processes 57
  - 3.2.2 The Spreading Coefficient Predicts Wetting of One Liquid by Another 58
- 3.3 The Young-Laplace Equation Relates Pressure Differences to Curvature across a Surface 60
  - 3.3.1 The Young-Laplace Equation Accounts for Capillary Rise 63
- 3.4 The Kelvin Equation Describes Vapor Pressure of Small Droplets and Explains Homogeneous Nucleation and Capillary Condensation 64
  - 3.4.1 The Kelvin Equation Describes the Critical Condition for Homogeneous Nucleation of Liquid Droplets from a Vapor 64
  - 3.4.2 Combining the Kelvin Equation and an Arrhenius Rate Equation Provides an Expression for the Rate of Homogeneous Nucleation 67
  - 3.4.3 Heterogeneous Nucleation Involves the Interfacial Free Energy between the New Phase and the Substrate 69
  - 3.4.4 Due to Capillary Effects, Surface Energy Can Cause a Liquid to Condense on a Rough Surface Prior to Saturation in the Bulk Phase 69
- 3.5 Thermodynamic Equations That Include Surface Chemistry Contributions Provide a Fundamental Basis for Characterizing Fluid–Fluid Interface Behavior 71
  - 3.5.1 The Gibbs Model Provides a Powerful Basis for Analyzing Interface Phenomena by Dividing a System into Two Bulk Phases and an Infinitesimally Thin Dividing Interface 71
  - 3.5.2 The Gibbs Adsorption Equation Relates
    Surface Excess to Surface Tension and the
    Chemical Potential of the Solute 73

- 3.6 Monolayers Formed by Insoluble Amphiphiles
  Behave As a Separate Phase and Are Most Readily
  Characterized Using a Langmuir Balance 76
- 3.7 Thermodynamics of Ideal Solutions Provide a Fundamental Basis for Characterizing Adsorption in Fluid-Solid Systems 79
  - 3.7.1 Entropy of Mixing Provides the Basis for the Ideal Solution Model and Very Dilute Real Solutions 79
  - 3.7.2 Based on an Ideal Mixing Model, the
    Langmuir Equation Describes Adsorption of
    Fluids at Solid Surfaces 81
- 3.8 Transport Processes Play a Fundamental Role in Interfacial Process Engineering 84
  - 3.8.1 Viscosity and Fluid Flow Provide
    Understanding Necessary for Analyzing
  - Many Interfacial Processes 84

    3.8.2 Viscosities of Surface Films Can Be
    Described by a Two-Dimensional Form of
    Poisseuille's Equation and Measured Using
    a Modified Langmuir Balance 90
    - Particles Are Important for Many Interfacial Processes 91 3.8.4 Sedimentation Rate of Particles Depends on

Viscosity and Flow of Fluids Containing

Particle Size and Solution Viscosity 96
3.8.5 Material Transport in Many Interfacial Processes Is Diffusion Controlled 98

Bibliography 103

3.8.3

Exercises 103

Appendix 3A Equations of Continuity and Motion 105 3A.1 Equation of Continuity 106

- 3A.2 Equation of Motion for a Fixed Control Volume 107
- 3A.3 Equation of Motion for a Moving Control Volume 111
- 3A.4 Flow Around a Sphere As an Example of Two-Dimensional Flow 112

#### 4 / Colloids 115

- 4.1 Colloidal Systems Are Thermodynamically Unstable, but Can Be Kinetically Stabilized by Steric or Electrostatic Repulsive Forces 121
- 4.2 Colloids Can Be Prepared in Two Ways 124
- 4.2.1 Preparation of Colloids by
  Precipitation—Nucleation and Growth
  Determine the Size, Shape, and
  Polydispersity of Colloids 124
  - 4.2.2 Colloids Also Can Be Prepared by Comminution 127

- 4.2.3 The Surfaces of Colloidal Particles Are Charged through Mechanisms Involving Surface Disassociation or Adsorption of Ionic Species 127
- 4.3 Charged Interfaces Play a Decisive Role in Many Interfacial Processes 129
  - 4.3.1 The Gouy-Chapman Theory Describes How a Charged Surface and an Adjacent Electrolyte Solution Interact 130
  - 4.3.2 The Electrical Double Layer Is Equivalent to a Capacitor—with One Electrode at the Particle Surface and the Other in the Electrolyte at a Distance Equal to the Debye Length 138
- 4.4 The Repulsive Potential Energy of Interaction,  $V_{\text{tep}}$ , between Two Identical Charged Surfaces in an Electrolyte Increases Exponentially as the Surfaces Move Together 140
  - 4.4.1 Repulsive Forces Originate Due to Electrostatic Interaction 140
  - 4.4.2 Repulsive Forces Also Originate Due to Osmotic Pressure 141
  - 4.4.3 The Total Repulsive Force between Two Charged Particles in an Electrolyte Is the Sum of the Electrostatic and the Osmotic Force 143
- 4.5 Electrostatic Stabilization of Colloidal Dispersions—Combining  $V_{att}$  and  $V_{rep}$  Leads to the DLVO Equation 145
  - 4.5.1 We Can Use the DLVO Theory to Determine the Conditions under Which Coagulation Becomes Rapid 146
  - 4.5.2 We Can Also Use the DLVO Theory to Determine the Rate at Which Colloidal Particles Coagulate 149
- 4.6 Surface Chemistry Plays an Important Role in Determining the Stability and Specific Properties of Colloidal Systems 152
  - 4.6.1 The Stern Model Provides a Way to Include Specific Ion Effects at Charged Interfaces 153
    4.6.2 The Zeta Potential Provides a Useful
  - 4.6.2 The Zeta Potential Provides a Useful Correlation between Double Layer Potentials and Colloid Stability 157
  - 4.6.3 In Colloidal Systems Many Specific Ion
    Effects Can Be Understood by the Action of
    Potential-Determining, Indifferent, and
    Charge-Reversing Ionic Constituents 157
  - 4.6.4 Heterocoagulation between Dissimilar
    Colloidal Particles Is More Complex Than
    Homocoagulation between Identical
    Particles 162

- Applications Involving Colloidal Interfacial Systems 163 4.7.1 Paints Exemplify Complex Interfacial Colloidal Systems 163 Protective Latex Coatings Are Formed 4.7.2 Using Diffusiophoresis-Movement of Colloidal Particles in the Gradient of a Chemical Solute 169 Modern Ceramics Place Stringent Demands 4.7.3 on Homogeneity and Quality Achievable through Colloidal Particle Processing 175 Zeolite Synthesis 182 4.7.4 Bibliography 188 Exercises 188 Appendix 4A The Complete Solution of the Poisson-Boltzmann Equation 190
  - Appendix 4B Calculations Illustrating Numerical Results with the Gouy-Chapman and the Stern Layer Equations 191
  - Appendix 4C Diffusion-Controlled Coagulation—Leading to Formation of Dimers 195
  - Appendix 4D Diffusion-Controlled

    Coagulation—Leading to Formation of

    Multimers 196

Appendix 4E Kinetics of Slow Coagulation 198

## 5 / Amphiphilic Systems—Liquid-Liquid Interfaces 201

- 5.1 Aggregation of Amphiphilic Molecules to Form Spherical Micelles Illustrates Many Features of Self-Organizing Systems 209
  - 5.1.1 Concentration of Amphiphilic Molecules in Solution Must Exceed a Critical Value Before Micelles Will Form 212
  - 5.1.2 The Radius of Spherical Micelles Is
    Determined by the Energy Balance between
    Unfavorable Hydrocarbon–Water
    Interaction and Polar Headgroup
    Coulombic Repulsion 214
  - 5.1.3 The Temperature Must Exceed a Critical Value Before Micelles Will Form 218
- 5.2 We Can Quantitatively Model Micelle Formation and Stability 219
  - 5.2.1 Amphiphile Assembly Can Be Modeled As a Reaction; the Equilibrium Constant Relates Exponentially to the Free Energy of Micellization 219
  - 5.2.2 The Free Energy of Micellization for lonic Micelles Contains Two

Components—Solvophobic Effects and
Headgroup Repulsion 221
The Contribution of Headgroup Interaction

5.2.3 to the Free Energy of Micellization Can Be Modeled Using the Gouy-Chapman

Theory 221

- The Behavior of Ionic Micelles Can Be 5.2.4Explained by Hydrocarbon Tail and
  - Headgroup Characteristics 223 Many Nonionic Micelles Separate into Two 5.2.5 Phases with Increasing Temperature 225
  - Relaxation Measurements Provide 5.2.6Information on Micellar Lifetimes and Dynamics 225
- Micelles Can Solubilize Other Hydrocarbon 5.2.7 Molecules 229
- Many Amphiphilic Molecules Form Bilayers, 5.3 Liquid Crystals, Vesicles, and Bicontinuous Structures 230
  - Surfactant Numbers Provide Useful Guides 5.3.1 for Predicting Different Aggregate Structures—Spherical Micelles, Cylindrical Micelles, and Bilayer Structures 230
  - Bilayers Are the Basic Building Blocks of a 5.3.2 Number of Amphiphilic Structures 232 Hydration and Thermal Undulatory 5.3.3 Interaction Forces Play an Important Role
    - in Stabilizing Bilayer Systems 232 Vesicles Are Molecular-Sized Containers
  - 5.3.4 Formed by the Breakup of Bilayers 236 Amphiphilic Bicontinuous Structures 5.3.5
  - Contain Two Coexisting Phases 238 Temperature Versus Concentration Phase 5.3.6 Diagrams for Amphiphilic Molecules in
  - Solution Are Complex 239 Micro- and Macroemulsions Are Homogeneous 5.4 Systems Containing Oil and Water Stabilized by Amphiphilic Molecules 240
    - The Curvature of the Oil-Water Interface 5.4.1 Can Be Manipulated 240
    - Microemulsions Are Thermodynamically 5.4.2 Stable Systems Possessing Microstructures with Characteristic Dimensions Less Than 100 nm 243
    - Macroemulsions Are Thermodynamically 5.4.3 Unstable Colloidal Systems Containing Oil (Water) Droplets Dispersed in Water (Oil) with Microstructure Dimensions Greater Than 100 nm 245
  - Applications Involving Amphiphilic Interfacial 3.5 Systems Illustrate the Rich Diversity of This Topic 248

- 5.5.1 Detergency is a Complex, Everyday Process Involving Surfactants 248
- 5.5.2 Pressure-Sensitive Adhesives Illustrate the Use of Emulsions in Interfacial Processes 257
- 5.5.3 Low-Density Foams Can Be Fabricated by Emulsion Polymerization 263

Bibliography 268
Exercises 268

## 6 / Polymers 271

- 6.1 Polymer Synthesis Produces Macromolecules That Are Generally Polydisperse 278
  - 6.1.1 Chain (Addition) Polymerization 279
  - 6.1.2 Step (Condensation) Polymerization 281

Produce Polydisperse Polymers 282

- 6.1.3 Both Chain and Step Polymerization
- 6.1.4 Polymers Are Used in Both Bulk and Solution Form 283
- 6.2 Bulk Solid Polymers Exist in Both the Amorphous and Crystalline State 283
  - 6.2.1 The Decrease in Young's Modulus with Increasing Temperature Marks Transitions from Crystalline Solid to Amorphous Glass to Rubbery Material to Viscous Fluid 284
  - 6.2.2 Many Crystalline Polymers Consist of Lamellar Structures That Form Spherulites 285
  - 6.2.3 Elastomers Are Crosslinked Polymer Systems above Their Glass Transition Temperature 286
  - 6.2.4 Mechanical Behavior of Bulk Polymer Solids 288
- 6.3 A Complete Description of Polymer Solutions Involves Integrating Information from Many Fields 289
  - 6.3.1 The Character of a Polymer Solution
    Changes with Concentration; There Are
    Three Different Concentration
    Regimes—Very Dilute, Semidilute, and
    Concentrated 289
  - 6.3.2 Macromolecule Conformation in Very Dilute Solution Depends on Molecular Weight and Solution Interaction 289
  - 6.3.3 The Crossover from Very Dilute to Semidilute to Concentrated Solution Behavior Depends on Chain Conformation 294
  - 6.3.4 The Regular Solution Model Provides the Basis for the Flory-Huggins Theory of Semidilute Polymer Solutions 295

- 6.4 Many Additional Features Affect Macromolecule Conformation in Solution 298
  - 6.4.1 Homopolymers with Amphiphilic

    Monomer Units Often Form Ordered

    Helical Structures—The DNA Double
    - Helix 299

      6.4.2 Heteropolymers Often Form Folded
    - Structures—Protein Chain Folding 300
      6.4.3 Block Copolymers Can Be Amphiphilic and
    - Show the Same Self-Assembly Properties as Surfactants 302
    - 6.4.4 Polyelectrolyte Chains Have a More Extended Conformation Because They Are Charged 304
- 6.4.5 Polymers Can Form Gels through Chemical Crosslinking and Self-Association 304
   8.5 Polymer Adsorption at Surfaces Plays an Important Role in Stabilizing Interfacial Systems 306
- 6.5.1 Polymers Can Be Attached to a Surface by Spontaneous Adsorption or Grafting 306
  6.5.2 Kinetics Often Determine the Outcome of a
  - Polymer Adsorption Process 309
    6.5.3 Adsorbed Polymers Drastically Change
    Forces between Surfaces—They Can
  - Lead to Colloidal Stabilization or Flocculation 309
    6.5.4 Polyelectrolytes Can Be Used to Flocculate
  - 6.5.5 Polymers Can Facilitate the Self-Assembly of Surfactants 313
- 6.6 Transport Properties of Homopolymer Solutions
  Can Change by Orders of Magnitude with Variation
  in Molecular Weight, Concentration, and
  Temperature 315
  - 6.6.1 In Dilute Polymer Solutions, Viscosity Scales with Molecular Weight to a Power between 0.5 and 1.0 316
  - between 0.5 and 1.0 316
    6.6.2 In Dilute Polymer Solutions, Diffusion
    Scales Inversely with Molecular Weight to a
  - Power between 0.5 and 1.0 319
    6.6.3 The de Gennes Reptation Model Describes
    Viscosity and Diffusion in Concentrated
  - Polymer Solutions and Polymer Melts 320
    6.6.4 The Mechanical Response of Polymer
    Systems Is Time Dependent—Polymers Are
    Viscoelastic Materials 324
  - 6.7 Processing of Polymeric Systems Illustrates How a Wide Variety of Materials Are Produced 325
    - 6.7.1 Production of Polyurethane Foams Involves Simultaneous Control of Polymerization and Foam Formation 325

- 6.7.2 High-Impact Polystyrene (HIPS) Is a Microphase Polymer Composite Consisting of Rubbery Particles Encased in a Brittle Thermoplastic 329
- 6.7.3 Thermoplastic Elastomers (TPEs) Are Block Copolymers That Are Thermoplastic at High Temperatures but Form Rubbery and Rigid Microphases on Cooling 334
- 6.7.4 Disposable Diapers Exemplify a Highly Engineered, Complex Polymer System 338

Bibliography 343

Exercises 343

Appendix 6A Regular Solution Theory 344

### 7 / Polymer Composites 347

- 7.1 The Composition, Processing, and Properties of Polymer Composites Are Unique 354
  - 7.1.1 The Typical Matrix Is a Thermoset or a Thermoplastic Polymer 354
  - 7.1.2 Reinforcements Are Either Particulates or Fibers 355
  - 7.1.3 Impregnation of the Reinforcements by the Matrix Can Be Complex—Good Wetting Is Critical 356
  - 7.1.4 Fiber-Matrix Interfacial Bonding Is Optimized for Strength and Toughness 358
- 7.2 Liquid-Solid Interfaces and Tortuosity Resist Flow between Fiber Reinforcements during Impregnation 360
  - 7.2.1 Impregnation under External Pressure Can Be Modeled as Flow through a Porous Medium—Darcy's Law 362
  - 7.2.2 Darcy's Law Predicts Impregnation Length as a Function of External Pressure 364
- 7.3 Capillary Action Also Assists Impregnation 367
  - 7.3.1 Capillary Flow Rate along Fibers Is Based on the Young-Laplace and Hagen-Poiseuille Equations 368
  - 7.3.2 Capillary Flow across Fibers Fluctuates
    Due to Varying Meniscus Curvature 370
  - 7.3.3 Flow Rates Due to External Pressure and Capillary Pressure Are Complementary 372
  - 7.3.4 Unequal Flow Rates and Changes in Dynamic Contact Angle Promote Voids 372
- 7.4 Interfacial Bond Strength Can Be Manipulated by Chemical and Mechanical Treatments 374
  - 7.4.1 Interfacial Bond Strength Is Key to the Mechanical Behavior of Polymer Composites 374
  - 7.4.2 Impact Strength Depends on Characteristics of the Matrix and the Interface 376

7.4.3	Fiber-Matrix Interface Bond Strength Is Controlled by Various Surface Treatments	377
7.4.4	Fiber–Matrix Interfacial Bond Strength Is Measured by Direct or Indirect Techniques	380

- 7.5 Polymer Composite Mechanical Properties Depend on Fiber Reinforcement, Matrix Properties, and Interfacial Bond Strength 382
  - 7.5.1 The Elastic Properties of Fiber-Reinforced Composites 383
  - 7.5.2 The Tensile Strength of Fiber-Reinforced Composites 388
- 7.6 Special Issues in the Processing and Application of Reinforced Composites 391
  - 7.6.1 Electric Cable Trays for the Eurotunnel Are Processed by the Pultrusion Technique 391
  - 7.6.2 Composite Field Repair 393

Bibliography 396

Exercises 397

## 8 / Liquid Coating Processes 399

- 8.1 Making Self-Adhesive Paper Labels: A Tutorial on the Fundamental Aspects of Coating Processes 404
  - 8.1.1 Adhesive Is Applied to the Backing Using Slot Coating 406
  - 8.1.2 Analysis of the Stability of the Slot Coating Process 407
- 8.2 Overview of Coating Methods 419
  - 8.2.1 Coating Methods May Be Classified
    According to Delivery Procedure 419
  - 8.2.2 Many Factors Are Involved in the Selection of a Coating Method 423
  - 8.2.3 Defects in Coatings 427
  - 8.2.4 Real-Time Imaging Has Been Applied to On-Line Web Inspection for Defects 429
- 8.3 Environmental Issues in Coating Processes 433
  - 8.3.1 Overview of the Clean Air Act Amendments of 1990 434
  - 8.3.2 Impact on the Coating Industry 434
- 8.4 Coating Technology Is Widespread 435
  - 8.4.1 Printing Is a Selected-Area Coating Process 435
  - 8.4.2 Photographic Films Are Manufactured by Multilayer Coatings of Photographic Emulsions 437
  - 8.4.3 Magnetic Recording Tapes Are Prepared by High-Speed Coating Processes 447

Bibliography 453

Appendix 8A Dynamics of Wetting and Spreading 454

8A.1 The Dynamic Contact Angle Is Always Greater Than the Static Contact Angle 454

#### 8A.2 Physical Understanding of the Dynamic Contact Angle is Complex 456

## 9 / General Properties of Crystalline Solid Surfaces 457

- 9.1 Crystalline Solids Consist of a Regular Array of Atoms 464
  - 9.2.1 Each Crystalline Material Is Defined by Its Unit Cell and Lattice Parameters 464
  - 9.1.2 Inert Gas Solids Are Composed of Close-Packed Arrays of Spherical Molecules Bonded by Dispersion Forces 466
  - 9.1.3 Ionic Solids, Basic to Many Ceramics, Are Composed of Different-Sized Positive and Negative Ions Bonded by Coulombic Forces 468
  - 9.1.4 Covalent Bonding Plays a Key Role in
    Determining the Structure of Many
    Materials Used in Electronic Devices, Such
    as Diamond and the III-IV and II-VI
    Compounds 471
  - 9.1.5 The Special Properties of Metals Arise from the Metallic Bond in Which Valence Electrons Are Shared by All Atoms 473
  - 9.1.6 Molecular Solids Exhibit Mixed Bonding 473
- 9.2 Characteristics of the Free Solid Surface 474
  - 9.2.1 The Free Surface Energy Equals One-Half the Cohesive Energy 474
  - 9.2.2 The Free Solid Surface Has a Structure Other Than That Rendered by Simple Dissection of the Material into Two Halves 482
- 9.3 The High Surface Energy of a Crystalline Solid Is Reduced through a Change in the Chemical Composition of the Surface 486
  - 9.3.1 Adsorption Reduces Surface Energy at Low Temperatures 487
  - 9.3.2 Segregation Reduces Surface Energy at High Temperatures 490
- 9.4 Crystalline Solids Contain Many Kinds of Imperfections 491
  - 9.4.1 Point Imperfections Exist in Thermodynamic Equilibrium 491
  - 9.4.2 Linear Imperfections, Known as Dislocation Lines, Are Always Present in Crystalline Solids 496
  - 9.4.3 Small-Angle Boundaries Are Planar Imperfections; They Are Formed from Arrays of Dislocations 501
- 9.5 Kinetic Transport Mechanisms Are Key to Formation, Processing, and Stability of Interfaces in Solid–Solid Systems 505

		9.5.1	Self-Diffusion and Solute Diffusion in Substitutional Solid Solutions by the Vacancy Mechanism 505	
		9.5.2	Self-Diffusion and Solute Diffusion in Interstitial Solid Solutions by the Interstitial Mechanism 510	
		9.5.3	Diffusion and Absolute Mobility Are Related by the Nernst-Einstein Equation 512	
		9.5.4	Fick's Second Law Describes Changes in Composition with Time 513	
		9.5.5	Large Differences in Diffusivity Lead to Movement of Interfacial Boundaries with Time and the Formation of Interfacial Defects 515	
		9.5.6	Diffusion over Surfaces Is Faster Than through the Bulk of the Material 516	
		9.5.7	Material Transport in Solids Also Can Be Driven by Electrical Potential Gradients and Mechanical Strain Gradients 518	
	Biblio	graphy	522	
	Exerc	ises 5.	22	
	Appe		A Miller Indexing System for Dencting ions and Planes in Single Crystals 524	
10	/ 201	hin Fi	lms—Solid-Solid Interfaces	
10	Processed from the Vapor Phase 527			
10.1 Ideal Gas Behavior Can Describe the Propertie of the Vapor Phase under Most Vacuum Conditions 535		e Vapor Phase under Most Vacuum		
		10.1.1	Gas (Vapor)-Phase Equation of State 535	
		10.1.2	Kinetic Behavior of Gas Molecules 536	
		10.1.3	Mean Free Path between Collisions 538	
		10.1.4	Impingement Flux—The Number of Particles Striking a Unit Area of Surface per Unit Time 539	
		10.1.5	Other Properties of Gases in Vacuum Are Sensitive to the Pressure 540	
	10.2	Choi	Practical Purposes, We Can Relate the ce of Vacuum System to the Kinetic Theory of s 540	
		10.2.1	Vacuum Pumps: Speed and Throughput 540	
		10.2.2	Angular Distribution of Emitted Molecules 543	
		10.2.3	Vacuum Chambers Come in a Variety of Materials and Shapes 544	
	10.3	Phy: High	sical Vapor Deposition Generally Employs 1-Vacuum Techniques 544	
		10.3.1	Physical Vapor Deposition by Thermal Evaporation—Molecules Are Evaporated from a Thermally Heated Source 545	

10.3.2	Physical Vapor Deposition by Sputtering— Ion Bombardment Ejects Molecules from a Source 550		
10.3.3	Other Physical Vapor Deposition Techniques Combine Features from Thermal and Sputtering Methods 555		
10.3.4	Substrates Must Be Carefully Prepared for Physical Vapor Deposition 556		
10.3.5	Deposition Rate and Thickness Can Be Monitored inside the Vacuum 557		
	cal Vapor Deposition Generally Employs		
Low-Va	scuum Techniques 557		
10.4.1	Higher Operating Pressures Means CVD Gives Conformal Coatings 558		
10.4.2	Precursor Sources for Chemical Vapor Deposition Are Vapors, Liquids, or Solids 559		
10.4.3	Some Typical Chemical Vapor Deposition Reactions 559		
10.4.4	Reactor Design and Substrate Heating 562		
10.4.5	Plasmas and Lasers Stimulate Reaction at Lower Temperatures 564		
10.4.6	Techniques Are Needed to Monitor CVD Deposition Processes 564		
10.4.7	For Certain CVD Systems, Safety Is an Important Issue 565		
Epitaxi Require	al Growth on Single Crystal Substrates es Special Deposition Conditions 566		
10.5.1	Molecular Beam Epitaxy Uses Evaporation under UHV Conditions 567		
10.5.2	Molecular Beam Sources 568		
10.5.3	Substrate Preparation and Temperature Control 569		
10.5.4	Thickness Monitoring and Surface Analysis 570		
10.5.5	Metallorganic Chemical Vapor Deposition Is an Alternative Technique for Processing Multilayer Epitaxial Thin Films 571		
Vapor-Phase Growth Mechanisms 521			
10.6.1	Capillarity Theory Describes Homogeneous and Heterogeneous Nucleation from the Vapor 572		
10.6.2	Thin-Film Growth Kinetics Involves a Combination of Mass Transfer, Surface Adsorption, Desorption, and Surface Reaction Steps 576		
10.6.3	Growth Modes and Microstructures of Thin Films Result from One of Three Basic Mechanisms 585		
	ections and Failure Mechanisms in Thin 598		

10.4

10.5

10.6

10.7

	10	0.7.1	Failure of Epitaxial Interfaces Is Primarily Due to Mechanical Strain 598
	10		Residual Stresses Induce Failure of Interphase Interfaces 601
	10	0.7.3	Mechanical Stresses Due to Impact and Friction Cause Failure in Service 605
	1	0.7.4	Thin-Film to Substrate Adhesion Is Important but Difficult to Measure 606
	1	0.7.5	Interface Failure Due to Surface Diffusion and Interdiffusion 608
	1	0.7.6	Porosity of a Film 609
	10.8	Thin-F	ilm Applications 610
	1	0.8.1	Magneto-Optical Data Storage Disks 610
	1	0.8.2	Thin-Film Infrared Sensors 617
	Bibliog	graphy	620
	Exercis	ses 620	•
11			oundary Surfaces and Interfaces alline Solids 623
	11.1	from th	Boundaries Form during Condensation ne Vapor, during Solidification from the or by Solid-State Recrystallization 628
	11.2	In Puro of Grai	e Polycrystalline Solids, the Surface Energy in Boundaries Gives Rise to Curvature and Grain Boundary Motion 630
		11.2.1	Grain Boundary Misorientation Is Represented by Tilt and Twist Components or by the Inverse of the Coherent Lattice Site Density 630
		11.2.2	Grain Boundary Surface Energy Is Determined by the Density of Unsatisfied Bonds and Related to Misorientation 633
		11.2.3	Grain Boundary Surface Energy Also

Varies with the Boundary Plane 636 Grain Boundary Surface Energy Lowers

Minimizing Grain Boundary Surface

Energy Determines the Equilibrium Configuration of Grain Boundary

Boundary Decohesion 637

Average Grain Size 639

Solute Atoms (or Impurities) Segregate

hinctions 638

the Cohesive Strength of a Solid-Grain

Grain Boundary Curvature Causes Grain

Boundary Movement and Increases the

Grain Boundary Surfaces Act as the

Source and Sink for Vacancies; As a Result, Grain Boundary Surfaces in Ionic Solids Can Become Charged 645

Preferentially in the Grain Boundary Region 645

11,2.4

11.2.5

11.2.6

11.2.7

11.3

- 11.3.1 Solute Atoms Segregate at Grain
  Boundaries to Reduce the Chemical,
  Mechanical, or Electrical Energy of the
  System 645
- 11.3.2 Impurity Segregation Is Used to Control Grain Growth 647
- 11.3.3 Impurity Segregation Modifies the Properties of Metals and Ceramics 648
- 11.4 Grain Boundary Surfaces in Equilibrium with Other Phases Lead to Different Microstructural Configurations 649
  - 11.4.1 Grain Boundary/Vapor-Phase Interaction Leads to Thermal Grooving 650
  - 11.4.2 Grain Boundary/Liquid-Phase Interaction Leads to Two-Phase Microstructures of Varying Complexity 651
  - 11.4.3 Grain Boundaries between Mixed Solid Phases Lead to Unusual Microstructures 656
- 11.5 Grain Boundaries Form Preferential Sites for Solid-State Precipitation Reactions 658
  - 11.5.1 Most Technologically Significant
    Crystalline Solids Undergo Phase
    Transformations and Precipitation at Low
    Temperatures 658
  - 11.5.2 Regular Solution Theory Describes Solid Solution Stability 658
  - 11.5.3 Heterogeneous Nucleation Theory
    Describes Initiation of Solid-State
    Precipitation 659
  - 11.5.4 Precipitate Particles Form from the Matrix Phase in Different Ways 661
- 11.6 Grain Boundary Devices Called Ceramic Varistors Protect Electrical Circuits from Voltage Surges 664

Bibliography 667

Exercises 667

- Appendix 11A Mechanical Behavior of Materials under Stress—Macroscopic View 669
- 11A.1 Elastic Deformation 669
- 11A.2 Fracture and Plastic Deformation 671
- 11A.3 Elastomer Deformation 673
- 11A.4 Time-Dependent Behavior—Viscoelastic Deformation 673
- Appendix 11B Mechanical Behavior of Materials under Stress—Microscopic View 678
- 11B.1 Elastic Deformation 678
- 11B.2 Plastic Deformation at Low Temperatures 679
- 11B.3 Plastic Deformation at High Temperatures 680
- 11B.4 Brittle Fracture 881