

Contents

<i>Preface</i>	<i>page xv</i>
<i>Acknowledgements</i>	xxi
<i>Notes on Units, Scales and Conventions</i>	xxiv
Part one: Thinking About the Material World	1
1 Idealizing Material Response	3
1.1 A Material World	3
1.1.1 Materials: A Databook Perspective	3
1.1.2 The Structure–Properties Paradigm	8
1.1.3 Controlling Structure: The World of Heat and Beat	12
1.2 Modeling of Materials	14
1.2.1 The Case for Modeling	14
1.2.2 Modeling Defined: Contrasting Perspectives	15
1.2.3 Case Studies in Modeling	18
1.2.4 Modeling and the Computer: Numerical Analysis vs Simulation	25
1.3 Further Reading	26
2 Continuum Mechanics Revisited	29
2.1 Continuum Mechanics as an Effective Theory	29
2.2 Kinematics: The Geometry of Deformation	31
2.2.1 Deformation Mappings and Strain	32
2.2.2 Geometry of Rigid Deformation	35
2.2.3 Geometry of Slip and Twinning	36
2.2.4 Geometry of Structural Transformations	37
2.3 Forces and Balance Laws	39
2.3.1 Forces Within Continua: Stress Tensors	39
2.3.2 Equations of Continuum Dynamics	41
2.3.3 Configurational Forces and the Dynamics of Defects	44
2.4 Continuum Descriptions of Deformation and Failure	51
2.4.1 Constitutive Modeling	51

viii	<i>Contents</i>	
2.4.2	Linear Elastic Response of Materials	51
2.4.3	Plastic Response of Crystals and Polycrystals	54
2.4.4	Continuum Picture of Fracture	60
2.5	Boundary Value Problems and Modeling	64
2.5.1	Principle of Minimum Potential Energy and Reciprocal Theorem	64
2.5.2	Elastic Green Function	66
2.5.3	Method of Eigenstrains	69
2.5.4	Numerical Solutions: Finite Element Method	72
2.6	Difficulties with the Continuum Approach	75
2.7	Further Reading	76
2.8	Problems	78
3	Quantum and Statistical Mechanics Revisited	81
3.1	Background	81
3.2	Quantum Mechanics	82
3.2.1	Background and Formalism	82
3.2.2	Catalog of Important Solutions	87
3.2.3	Finite Elements and Schrödinger	94
3.2.4	Quantum Corrals: A Finite Element Analysis	101
3.2.5	Metals and the Electron Gas	103
3.2.6	Quantum Mechanics of Bonding	109
3.3	Statistical Mechanics	115
3.3.1	Background	115
3.3.2	Entropy of Mixing	119
3.3.3	The Canonical Distribution	122
3.3.4	Information Theoretic Approach to Statistical Mechanics	126
3.3.5	Statistical Mechanics Models for Materials	129
3.3.6	Bounds and Inequalities: The Bogoliubov Inequality	135
3.3.7	Correlation Functions: The Kinematics of Order	137
3.3.8	Computational Statistical Mechanics	139
3.4	Further Reading	142
3.5	Problems	144
	Part two: Energetics of Crystalline Solids	147
4	Energetic Description of Cohesion in Solids	149
4.1	The Role of the Total Energy in Modeling Materials	149
4.2	Conceptual Backdrop for Characterizing the Total Energy	152
4.2.1	Atomistic and Continuum Descriptions Contrasted	152

	<i>Contents</i>	ix
4.2.2	The Many-Particle Hamiltonian and Degree of Freedom Reduction	154
4.3	Pair Potentials	156
4.3.1	Generic Pair Potentials	156
4.3.2	Free Electron Pair Potentials	158
4.4	Potentials with Environmental and Angular Dependence	164
4.4.1	Diagnostics for Evaluating Potentials	164
4.4.2	Pair Functionals	165
4.4.3	Angular Forces: A First Look	172
4.5	Tight-Binding Calculations of the Total Energy	176
4.5.1	The Tight-Binding Method	176
4.5.2	An Aside on Periodic Solids: k -space Methods	184
4.5.3	Real Space Tight-Binding Methods	189
4.6	First-Principles Calculations of the Total Energy	197
4.6.1	Managing the Many-Particle Hamiltonian	198
4.6.2	Total Energies in the Local Density Approximation	200
4.7	Choosing a Description of the Total Energy: Challenges and Conundrums	203
4.8	Further Reading	204
4.9	Problems	206
5	Thermal and Elastic Properties of Crystals	210
5.1	Thermal and Elastic Material Response	210
5.2	Mechanics of the Harmonic Solid	213
5.2.1	Total Energy of the Thermally Fluctuating Solid	214
5.2.2	Atomic Motion and Normal Modes	216
5.2.3	Phonons	228
5.2.4	Buckminsterfullerene and Nanotubes: A Case Study in Vibration	229
5.3	Thermodynamics of Solids	231
5.3.1	Harmonic Approximation	231
5.3.2	Beyond the Harmonic Approximation	239
5.4	Modeling the Elastic Properties of Materials	244
5.4.1	Linear Elastic Moduli	244
5.4.2	Nonlinear Elastic Material Response: Cauchy–Born Elasticity	248
5.5	Further Reading	250
5.6	Problems	251
6	Structural Energies and Phase Diagrams	253
6.1	Structures in Solids	253
6.2	Atomic-Level Geometry in Materials	254

x	<i>Contents</i>	
6.3	Structural energies of solids	260
6.3.1	Pair Potentials and Structural Stability	261
6.3.2	Structural Stability in Transition Metals	264
6.3.3	Structural Stability Reconsidered: The Case of Elemental Si	265
6.4	Elemental Phase Diagrams	268
6.4.1	Free Energy of the Crystalline Solid	268
6.4.2	Free Energy of the Liquid	275
6.4.3	Putting It All Together	277
6.4.4	An Einstein Model for Structural Change	278
6.4.5	A Case Study in Elemental Mg	280
6.5	Alloy Phase Diagrams	282
6.5.1	Constructing the Effective Energy: Cluster Expansions	283
6.5.2	Statistical Mechanics for the Effective Hamiltonian	291
6.5.3	The Effective Hamiltonian Revisited: Relaxations and Vibrations	297
6.5.4	The Alloy Free Energy	299
6.5.5	Case Study: Oxygen Ordering in High T_C Superconductors	300
6.6	Summary	304
6.7	Further Reading	304
6.8	Problems	305
	Part three: Geometric Structures in Solids: Defects and Microstructures	309
7	Point Defects in Solids	311
7.1	Point Defects and Material Response	311
7.1.1	Material Properties Related to Point Disorder	312
7.2	Diffusion	318
7.2.1	Effective Theories of Diffusion	318
7.3	Geometries and Energies of Point Defects	326
7.3.1	Crystallographic Preliminaries	327
7.3.2	A Continuum Perspective on Point Defects	328
7.3.3	Microscopic Theories of Point Defects	332
7.3.4	Point Defects in Si: A Case Study	341
7.4	Point Defect Motions	344
7.4.1	Material Parameters for Mass Transport	345
7.4.2	Diffusion via Transition State Theory	346
7.4.3	Diffusion via Molecular Dynamics	351
7.4.4	A Case Study in Diffusion: Interstitials in Si	353
7.5	Defect Clustering	356

<i>Contents</i>		xi
7.6	Further Reading	356
7.7	Problems	359
8	Line Defects in Solids	362
8.1	Permanent Deformation of Materials	362
8.1.1	Yield and Hardening	363
8.1.2	Structural Consequences of Plastic Deformation	365
8.1.3	Single Crystal Slip and the Schmid Law	367
8.2	The Ideal Strength Concept and the Need for Dislocations	369
8.3	Geometry of Slip	371
8.3.1	Topological Signature of Dislocations	372
8.3.2	Crystallography of Slip	375
8.4	Elastic Models of Single Dislocations	382
8.4.1	The Screw Dislocation	382
8.4.2	The Volterra Formula	388
8.4.3	The Edge Dislocation	391
8.4.4	Mixed Dislocations	392
8.5	Interaction Energies and Forces	393
8.5.1	The Peach–Koehler Formula	395
8.5.2	Interactions and Images: Peach–Koehler Applied	398
8.5.3	The Line Tension Approximation	402
8.6	Modeling the Dislocation Core: Beyond Linearity	404
8.6.1	Dislocation Dissociation	404
8.6.2	The Peierls–Nabarro Model	406
8.6.3	Structural Details of the Dislocation Core	412
8.7	Three-Dimensional Dislocation Configurations	415
8.7.1	Dislocation Bow-Out	416
8.7.2	Kinks and Jogs	418
8.7.3	Cross Slip	423
8.7.4	Dislocation Sources	426
8.7.5	Dislocation Junctions	430
8.8	Further Reading	435
8.9	Problems	437
9	Wall Defects in Solids	441
9.1	Interfaces in Materials	441
9.1.1	Interfacial Confinement	442
9.2	Free Surfaces	446
9.2.1	Crystallography and Energetics of Ideal Surfaces	447
9.2.2	Reconstruction at Surfaces	452
9.2.3	Steps on Surfaces	474

xii	<i>Contents</i>	
9.3	Stacking Faults and Twins	476
9.3.1	Structure and Energetics of Stacking Faults	477
9.3.2	Planar Faults and Phase Diagrams	484
9.4	Grain Boundaries	487
9.4.1	Bicrystal Geometry	489
9.4.2	Grain Boundaries in Polycrystals	492
9.4.3	Energetic Description of Grain Boundaries	494
9.4.4	Triple Junctions of Grain Boundaries	500
9.5	Diffuse Interfaces	501
9.6	Modeling Interfaces: A Retrospective	502
9.7	Further Reading	503
9.8	Problems	505
10	Microstructure and its Evolution	507
10.1	Microstructures in Materials	508
10.1.1	Microstructural Taxonomy	508
10.1.2	Microstructural Change	516
10.1.3	Models of Microstructure and its Evolution	519
10.2	Inclusions as Microstructure	520
10.2.1	Eshelby and the Elastic Inclusion	520
10.2.2	The Question of Equilibrium Shapes	527
10.2.3	Precipitate Morphologies and Interfacial Energy	528
10.2.4	Equilibrium Shapes: Elastic and Interfacial Energy	529
10.2.5	A Case Study in Inclusions: Precipitate Nucleation	537
10.2.6	Temporal Evolution of Two-Phase Microstructures	540
10.3	Microstructure in Martensites	546
10.3.1	The Experimental Situation	547
10.3.2	Geometrical and Energetic Preliminaries	551
10.3.3	Twinning and Compatibility	554
10.3.4	Fine-Phase Microstructures and Attainment	560
10.3.5	The Austenite–Martensite Free Energy Reconsidered	565
10.4	Microstructural Evolution in Polycrystals	566
10.4.1	Phenomenology of Grain Growth	567
10.4.2	Modeling Grain Growth	568
10.5	Microstructure and Materials	580
10.6	Further Reading	580
10.7	Problems	582
	Part four: Facing the Multiscale Challenge of Real Material Behavior	585

<i>Contents</i>		xiii
11	Points, Lines and Walls: Defect Interactions and Material Response	587
11.1	Defect Interactions and the Complexity of Real Material Behavior	587
11.2	Diffusion at Extended Defects	588
11.2.1	Background on Short-Circuit Diffusion	588
11.2.2	Diffusion at Surfaces	589
11.3	Mass Transport Assisted Deformation	592
11.3.1	Phenomenology of Creep	593
11.3.2	Nabarro–Herring and Coble Creep	595
11.4	Dislocations and Interfaces	599
11.4.1	Dislocation Models of Grain Boundaries	600
11.4.2	Dislocation Pile-Ups and Slip Transmission	604
11.5	Cracks and Dislocations	609
11.5.1	Variation on a Theme of Irwin	610
11.5.2	Dislocation Screening at a Crack Tip	611
11.5.3	Dislocation Nucleation at a Crack Tip	615
11.6	Dislocations and Obstacles: Strengthening	620
11.6.1	Conceptual Overview of the Motion of Dislocations Through a Field of Obstacles	622
11.6.2	The Force Between Dislocations and Glide Obstacles	625
11.6.3	The Question of Statistical Superposition	628
11.6.4	Solution Hardening	633
11.6.5	Precipitate Hardening	636
11.6.6	Dislocation–Dislocation Interactions and Work Hardening	642
11.7	Further Reading	644
11.8	Problems	647
12	Bridging Scales: Effective Theory Construction	649
12.1	Problems Involving Multiple Length and Time Scales	651
12.1.1	Problems with Multiple Temporal Scales: The Example of Diffusion	652
12.1.2	Problems with Multiple Spatial Scales: The Example of Plasticity	653
12.1.3	Generalities on Modeling Problems Involving Multiple Scales	655
12.2	Historic Examples of Multiscale Modeling	658
12.3	Effective Theory Construction	668
12.3.1	Degree of Freedom Selection: State Variables, Order Parameters and Configurational Coordinates	669
12.3.2	Dynamical Evolution of Relevant Variables: Gradient Flow Dynamics and Variational Principles	674
12.3.3	Inhomogeneous Systems and the Role of Locality	685

xiv	<i>Contents</i>	
	12.3.4 Models with Internal Structure	688
	12.3.5 Effective Hamiltonians	697
12.4	Bridging Scales in Microstructural Evolution	701
	12.4.1 Hierarchical Treatment of Diffusive Processes	701
	12.4.2 From Surface Diffusion to Film Growth	709
	12.4.3 Solidification Microstructures	711
	12.4.4 Two-Phase Microstructures Revisited	715
	12.4.5 A Retrospective on Modeling Microstructural Evolution	718
12.5	Bridging Scales in Plasticity	719
	12.5.1 Mesoscopic Dislocation Dynamics	720
	12.5.2 A Case Study in Dislocations and Plasticity: Nanoindentation	728
	12.5.3 A Retrospective on Modeling Plasticity Using Dislocation Dynamics	731
12.6	Bridging Scales in Fracture	732
	12.6.1 Atomic-Level Bond Breaking	732
	12.6.2 Cohesive Surface Models	734
	12.6.3 Cohesive Surface Description of Crack Tip Dislocation Nucleation	735
12.7	Further Reading	736
12.8	Problems	738
13	Universality and Specificity in Materials	742
13.1	Materials Observed	743
	13.1.1 What is a Material: Another Look	743
	13.1.2 Structural Observations	744
	13.1.3 Concluding Observations on the Observations	746
13.2	How Far Have We Come?	748
	13.2.1 Universality in Materials	749
	13.2.2 Specificity in Materials	750
	13.2.3 The Program Criticized	751
13.3	Intriguing Open Questions	752
13.4	In Which the Author Takes His Leave	754
	<i>References</i>	757
	<i>Index</i>	771