## Crystals, Defects and Microstructures

**Modeling Across Scales** 

### ROB PHILLIPS

Brown University, Providence RI



ISBN 0 521 79005 0 (hardback)

# Crystals, Defects and Microstructures Modeling Across Scales

#### **ROB PHILLIPS**

Brown University, Providence RI



### Contents

Prefe	ace	page	? XV
Ackn	iowledge	ements	xxi
Note	s on Un	its, Scales and Conventions · x	xiv
Part	t one: T	Thinking About the Material World	1
1	Ideali	zing Material Response	3
1.1	A Mat	erial 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	Model	ing 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	Furthe	r Reading	26
2	Conti	nuum Mechanics Revisited	29
2.1	Contin	nuum Mechanics as an Effective Theory	29
2.2	Kinem	natics: 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	Contir	nuum Descriptions of Deformation and Failure	51
	2 4 1	Constitutive Modeling	51

viii Contents

	2.4.2	Linear Elastic Response of Materials	51
	2.4.2	Plastic Response of Crystals and Polycrystals	54
	2.4.4	Continuum Picture of Fracture	60
2.5		lary Value Problems and Modeling	64
2.5	2.5.1	Principle of Minimum Potential Energy and Reciprocal	04
	2.3.1	Theorem	64
	2.5.2		66
		Method of Eigenstrains	69
	2.5.4	Numerical Solutions: Finite Element Method	72
2.6		ulties with the Continuum Approach	75
2.7		or Reading	75 76
2.8	Proble	-	78
2.0	110010		
3	Quan	tum and Statistical Mechanics Revisited	81
3.1	Backg		81
3.2	_	um Mechanics	82
	3.2.1	Background and Formalism	82
	3.2.2		87
	3.2.3	Č	94
	3.2.4	,	101
	3.2.5	Metals and the Electron Gas	103
	3.2.6	Quantum Mechanics of Bonding	109
3.3	Statist	ical 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	Furthe	er Reading	142
3.5	Proble	ems	144
Par	t two: I	Energetics of Crystalline Solids	147
4	Energ	getic Description of Cohesion in Solids	149
4.1	The R	ole of the Total Energy in Modeling Materials	149
4.2	Conce	ptual Backdrop for Characterizing the Total Energy	152
	421	Atomistic and Continuum Descriptions Contrasted	152

Contents ix

	4.2.2	The Many-Particle Hamiltonian and Degree of Freedom	
		Reduction	154
4.3	Pair Po	otentials	156
	4.3.1	Generic Pair Potentials	156
	4.3.2	Free Electron Pair Potentials	158
4.4	Potent	ials 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-l	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-P	Principles Calculations of the Total Energy	197
	4.6.1	Managing the Many-Particle Hamiltonian	198
<b>1</b>	4.6.2	Total Energies in the Local Density Approximation	200
4.7	Choos	ing a Description of the Total Energy: Challenges and	
	Conun	drums	203
4.8	Furthe	r Reading	204
4.9	Proble	ms	206
5	Thern	nal and Elastic Properties of Crystals	210
5.1	Therm	al and Elastic Material Response	210
5.2	Mecha	nnics 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	Therm	odynamics of Solids	231
	5.3.1	Harmonic Approximation	231
	5.3.2	Beyond the Harmonic Approximation	239
5.4	Model	ing 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	Furthe	r Reading	250
5.6	Proble	ms	251
6	Struct	tural Energies and Phase Diagrams	253
6.1	Structi	ures in Solids	253
6.2	Atomic-Level Geometry in Materials		

x Contents

6.3	Structural energies of solids		
	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	Eleme	ental 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		
	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	Summ	ary	304
6.7	Furthe	er Reading	304
6.8	Proble	ems	305
Par	t three:	Geometric Structures in Solids: Defects and	
	rostruc		309
7	Point	Defects in Solids	311
7.1	Point 1	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	Geom	etries 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		
	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 3		

Contents xi

7.6	Further Reading		
7.7	Proble	ems	359
8	Line I	Defects in Solids	362
8.1	Permanent Deformation of Materials		
	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 Id	leal Strength Concept and the Need for Dislocations	369
8.3	Geometry of Slip		
	8.3.1	Topological Signature of Dislocations	372
	8.3.2	Crystallography of Slip	375
8.4	Elastic	c 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	Interac	ction 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	Model	ling 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	Furthe	er Reading	435
8.9	Proble	ems	437
9	Wall l	Defects in Solids	441
9.1	Interfa	aces 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 Contents

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	
	avior	585

Contents 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	Diffusi	on at Extended Defects	588
	11.2.1	Background on Short-Circuit Diffusion	588
	11.2.2	Diffusion at Surfaces	589
11.3	Mass T	ransport Assisted Deformation	592
	11.3.1	Phenomenology of Creep	593
	11.3.2	Nabarro-Herring and Coble Creep	595
11.4	Disloca	ations 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	Disloca	ations 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	Proble	ms	647
12	Rridgi	ng Scales: Effective Theory Construction	649
12.1	_	ms Involving Multiple Length and Time Scales	651
12.1		Problems with Multiple Temporal Scales: The Example of	031
	12.1.1	Diffusion —	652
	12 1 2	Problems with Multiple Spatial Scales: The Example of	052
	12.1.2	Plasticity	653
	12.1.3	Generalities on Modeling Problems Involving Multiple Scales	655
12.2		c Examples of Multiscale Modeling	658
12.3		ve Theory Construction	668
12.5		Degree of Freedom Selection: State Variables, Order	000
	12.0.1	Parameters and Configurational Coordinates	669
	12.3.2	Dynamical Evolution of Relevant Variables: Gradient Flow	507
	12.0.2	Dynamics and Variational Principles	674
	12.3.3	Inhomogeneous Systems and the Role of Locality	685

xiv Contents

		Models with Internal Structure	688
		Effective Hamiltonians	697
12.4	•	ng 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		
	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		
	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	Problem	ms	738
13	Univer	sality and Specificity in Materials	742
13.1	Materials Observed		
	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?		
	13.2.1	Universality in Materials	749
	13.2.2	Specificity in Materials	750
	13.2.3	The Program Criticized	751
13.3	Intrigu	ing Open Questions	752
13.4	_	ch the Author Takes His Leave	754
Refer	ences	P	757
Indov	•		771