# **Rob Phillips** CRYSTALS, DEFECTS AND MICROSTRUCTURES Modeling Across Scales



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#### Crystals, Defects and Microstructures

Materials science has emerged as one of the central pillars of the modern physical sciences and engineering, and is now even beginning to claim a role in the biological sciences. A central tenet in the analysis of materials is the structure–property paradigm, which proposes a direct connection between the geometric structures within a material and its properties.

The increasing power of high-speed computation has had a major impact on theoretical materials science and has permitted the systematic examination of this connection between structure and properties. In this textbook, Rob Phillips examines the various methods that have been used in the study of crystals, defects and microstructures and that have made such computations possible. The author presents many of the key general principles used in the modeling of materials, and punctuates the text with real case studies drawn from recent research. A second key theme is the presentation of recent efforts that have been developed to treat problems involving either multiple spatial or temporal scales simultaneously.

This text is intended for graduate students and researchers in science and engineering with an interest in the theoretical constructs that have been devised to undertake the study of materials.

# Crystals, Defects and Microstructures Modeling Across Scales

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### Preface

Materials science as a formal discipline has quietly emerged as one of the central pillars of the physical sciences. Whether one interests oneself in the creation of lighter, more durable surfboards, or in the invention of new technologies to free up the traffic jam on the world wide web, in the end, these questions will always imply demands which must be met by new classes of materials.

Though the study of materials is largely rooted in the enlightened empiricism of traditional metallurgy, the advent of high-speed computers and the emergence of robust quantum simulations suggests new engineering strategies in which mechanism-based understanding might be hoped to lead to new materials. As a result of the maturation of theoretical materials science, it has become increasingly possible to identify a corpus of central results which serve as the basis for the analysis of materials. In addition, increasingly complex materials with structures at many different scales have led to the emergence of methods built around the explicit consideration of multiple scales simultaneously. As a result of these advances, this book attempts to take stock of the present capacity for modeling materials, with the word modeling used in the broadest sense.

The book is divided into four basic parts. It opens with an overview of some of the key issues concerning materials that one might hope to succeed in modeling. Special reference is made to the notion of material parameters as characterized by the broad variety of data about materials that may be found in any databook. Though my comments on material response will be rather generic, my efforts to model such response will be restricted almost exclusively to *crystalline* solids. Though I am ashamed to have ignored so many classes of important and interesting materials, in the end, even restricting myself to crystalline materials left me with a project that exceeds my competence. After the introduction to material response, I present something like a modelers toolkit with a review of the key ideas from continuum mechanics, quantum mechanics and statistical mechanics that one might want to bring to the evaluation of a particular problem in the mechanics of materials. My argument here is that these three broad fields of study serve as the cornerstone for the rest of what we will do. The second main section of the

book is entitled 'Energetics of Crystalline Solids' and aims to describe the various tools that may be brought to bear on the problem of understanding the properties of perfect crystals. The argument made here is that the understanding we will require later concerning the role of defects in materials will have more impact when measured against the backdrop of the perfect solid. Particular emphasis in chaps. 4–6 is placed on computing the total energies of a given solid and using these energies to deduce the thermal and elastic properties of solids and the structural stability of different materials as revealed by phase diagrams. It should be noted that though I have restricted my attention to crystalline solids, much of what we will say in these chapters can be borrowed without alteration in the context of noncrystalline solids (and even liquids).

Part 3, 'Geometric Structures in Solids: Defects and Microstructures' is organized according to the dimensionality of the various defects that populate materials and considers point defects (chap. 7), line defects (chap. 8) and interfacial defects (chap. 9). The organization of the material along dimensional lines is in the end somewhat artificial, but provides an organizational thread which has been useful to me if not the reader. Once an understanding of these various defects is in hand, I make an attempt at describing the assembly of these defects into a material's microstructure (chap. 10). The final part of the book, 'Facing the Multiscale Challenge of Real Material Behavior', should be seen as the culmination of the efforts set forth in the preceding chapters with the aim being to see just how far the modeler can go in the attempt to concretely consider material behavior. In addition, I have had a go at trying to seek the generic features of those models in which a deliberate attempt has been made to eliminate degrees of freedom. Indeed, my contention is that the enormous current interest in 'multiscale modeling' is born in large part of a self-conscious attempt to construct theories in a way that will lend them computational efficiency. Though there has been an incontrovertible increase in computational power, it has carried with it an attendant perception that almost always our appetite will outstrip our abilities. As a result, modelers throughout the physical sciences have had to seek to reformulate existing theories and to create new ones in a way that is ever mindful of the need to reduce computational burden.

My reasons for writing this book are primarily selfish. I have found that the only way I can really learn something is by self-study, and in particular, by seeking understanding at the level of the details – factors of 2 and  $\pi$  included. I consider myself one of the lucky few, namely, those who are able to earn a living as a college professor. Indeed, my privileges are greater yet. Almost daily I count my good fortune for having landed in the Solid Mechanics group at Brown University. One of the challenges in entering such a group has been to grope my way to some modicum of understanding in the area of the mechanics of materials. This book represents one part of that groping and reflects my own sense of some of the key

strategies that may be brought to bear on modeling material behavior. As part of the process of bringing myself up to speed for attempting to write this book, I have also undertaken the writing of a number of review articles with which the perceptive reader will undoubtedly see some overlap. This process was intentional in the hope that by working with various coauthors a useful vision of much of the material included here could be built up. Similarly, many of the ideas set forth here have been tested out in courses given at Brown, Caltech, the National University of Singapore and the Institut National Polytechnique de Grenoble.

My intention in writing this book has not been to produce an encyclopedic compendium of all that is known concerning the modeling of materials and their properties. Rather, I have attempted to consider a sufficiently diverse set of problems to reveal the *habit of mind* that can be brought to the study of materials. Indeed, the book is largely anecdotal, with what I perceive to be fundamental ideas punctuated by more speculative 'case studies' that may not stand the test of time. As a result, the book has mixed character, alternating back and forth between text and monograph mode. In his outstanding book The Gift of Fire, Richard Mitchell notes the distinction between knowing and knowing about. The aims of the present work move back and forth between these objectives, with my hope being that after reading those sections having to do with general principles (and working the corresponding problems), the reader will 'know' these ideas. By way of contrast, the case studies are put forth more in the spirit of 'knowing about' with the hope that such studies will familiarize the reader with the implementation of the general ideas as well as the attendant literature, and will embolden him or her to set out to carry through a detailed case study themselves. I should also note that although many a preface emboldens the reader with the claim that various chapters can be read independently, I have written the present work very much as narrative, with the same idea presented in a different light several (or even many) different times, each contrasted with the other. For example, the discussion on Bridging Scales in Microstructural Evolution in chap. 12 presupposes a knowledge of what has gone before in chap. 10. Though it is true that one can read one without the other, it is certain that the message I wish to convey about microstructure and its evolution can only be gleaned by reading them both. For me, the book was written as a single entity and its logic is intertwined accordingly.

In keeping with this general philosophy, the book is populated by a minimum of numerical tables in which specific data are presented. Rather, I have opted for pictorial and graphical representation of numerical results with the aim being the presentation of trends rather than detailed quantitative insights. On the other hand, there are a number of instances in which I present tables of data, but in the more sympathetic form of pictures. The calculations of the group of Skriver come to mind in this regard since they have done the service of providing the energies of

a number of defects (vacancies - fig. 7.15, surfaces - fig. 9.5 and step energies - fig. 9.29) for a whole host of different materials, using the same theoretical analysis in each instance raising the possibility of a meaningful assessment of the trends. In addition, at times I have resorted to presenting collages of experimental data since I often feel it is beyond my competence to bring expert judgement to one experiment vs another and thus leave it to the reader to explore several sources and thereby decide for his or herself. My selection of material is also based in part upon a sinking feeling I sometimes get both while attending meetings and while cranking out the next calculation at my desk: it seems that so much of 'research' (mine included) is slated for obsolescence from the moment of its inception. It has always seemed to me that pedagogy is an ideal litmus test of significance. Is a particular piece of work something that I would want to tell my students? The difficulty in answering this question is further exacerbated by the pedagogical uncertainties that attend the increasing reliance on numerical solutions and computer simulation. How exactly are we to communicate what is being learned from computational approaches? I have tried to follow a basic formula in many of the later chapters in the book. An attempt is first made to illustrate the fundamental principles involved in contemplating a given class of material properties. These generic ideas, which are assumed to be largely uncontroversial, are then illustrated in an iterative fashion with a given case study examined from as many different angles as possible. For example, in discussing structural stability of Si, I make a point of showing how these questions can be addressed both from the perspective of empirical potentials and using first-principles quantum mechanical treatments. Similarly, in my treatment of grain growth, I show how the Potts model, phase field models and sharp interface models may all be used to examine the same basic process. My logic in these instances is to encourage a breadth of perspective filtered by a critical eye that sees the shortcomings of all of these approaches. In the end, this book reflects my quest to unearth some of the exciting developments in the modeling of thermomechanical properties which have the power to either instruct or predict or entertain.

In addition to commenting on what is in this book, it is with a trace of sadness that I also note what is not. With the narrowing of time between a given day of writing and the date of my self-imposed deadline, as well as with the increasingly swollen zip disks and hard copies of my book, it became increasingly clear that I must abandon many of my original intentions and resort to wholesale slashing. It is with particular regret that I eliminated my discussions of thermal conductivity, electromigration, the use of path integral methods to study diffusion and the electronic structure of quantum dots. In the end, I came to the view that I must stop and return to more active daily participation in family, sleep and my own research. I should also note that despite its length, in the end experts will recognize that my book has provided only a caricature of their fields. My aim was to highlight what seemed to me to be either the most general ideas or the most intriguing from each broad area.

A word of explanation concerning references and further reading is in order. Ultimately, I decided to reference the works of others in only two ways. First, the *Further Reading* sections at the end of each chapter make reference only to those books or articles that form a part of my working and thinking vocabulary. Each time reference is made to one of these works, I attempt to provide some editorial comment as to why it has appeared on my list. My taste is idiosyncratic: if given the choice, I will always seek out that author who tells me something other than the party line, who has forged his or her own vision. I hold to this same mean in graduate teaching with the conviction that students are not interested in a watered down regurgitation of what they can read in the textbook – a unique perspective is what interests me.

In addition to the suggestions for further reading, I have also compiled a single bibliography at the end of the book. This list serves an entirely different purpose and there is only a single way to get on it. These books and articles are those from which I have borrowed figures, followed derivations or turned the analysis into a 'case study'. One of my abiding aims has been to try to figure out which part of the work on modeling has earned some level of permanence. Certain models (for example the quantum corral discussed in chap. 2) are pedagogically satisfying and at the same time permit immediate comparison with experiment. This is the ideal situation and, wherever possible, I have attempted to include them. In addition, I have also sought those steps forward that illustrate a certain approach that, in my opinion, should be imitated.

As is evident from the preceding paragraphs, my bibliographic acumen is severely limited. The reference list is not encyclopedic and reflects my taste for browsing the index in a few favorite journals such as *Physical Review B* and *Physical Review Letters, Journal of Mechanics and Physics of Solids, Metallurgical Transactions A, Philosophical Magazine* and *Acta Metallurgica.* I am a particular fan of the 'Overview' sections in *Acta Metallurgica* and the articles written by award recipients in *Metallurgical Transactions.* Further, my choice of references is biased in favor of friends and acquaintances, due largely to the fact that in these instances I have had the benefit of private discussions in order to learn what *really* happened. This is especially true in those cases where I sought a picture to illustrate a concept such as, for example, a polycrystalline microstructure. In these cases, it was most convenient to tap acquaintances, resulting in an over representation of work carried out at Brown. Hence, while my choice of references should be seen as a rejection of those that are not.

Another feature of the book deserving of comment is the problem sets that are to be found at the end of each chapter. Many of these problems have already had a tour of duty in the various courses that I have taught at Brown and Caltech. On the other hand, there is a reasonable fraction of these problems that have not seen the light of day before now and thus risk having bugs of various types. The problems come in all types ranging from the fleshing out of material covered in the chapters themselves to the construction of full-fledged computational solutions to problems that are otherwise not tractable.

A few stylistic comments are also in order. For the most part, I have written the book in the first person plural, making constant reference to 'we' this and 'we' that. My reason for selecting this language is an honest reflection of my presumed relation with the reader – I imagine us both, you the reader and me, side by side and examining each question as it arises, almost always in a questioning tone: can we do better? I have reserved the more personal and subjective 'I' for those places where it is really my opinion that is being espoused as, for example, in the sections on *Further Reading*. In addition, the book is written in an informal (and at times light) style with various asides and observations. I fear that I will probably be charged with both flippancy and arrogance, but wish to note at the outset that my hope was to produce a book that was to some extent fun to read. But even more importantly, I have tried to have fun in its writing. Three hours a morning for four years is a lot of hours to sit by oneself and I confess that on many occasions I could not resist certain turns of phrase or observations that amused *me*.

> Rob Phillips Barrington RI 2000

### Acknowledgements

As a voracious reader myself, I am a veteran of many a preface and its attendant list of acknowledgements. What I realize now that it is my turn to make such a list is that for one such as me, who owes so much to so many, acknowledgements are deeply felt and yet are probably irrelevant to the anonymous reader. As said above, I wrote this book largely for myself in the hope that I would learn something in the act of so doing. This learning can be divided along two main lines, one emanating from the isolated groping I did at my desk, and the other from the pleasant meaningful interactions I have had with the people it is the business of this section to acknowledge. These paragraphs are for me and my family, my friends and my teachers. To all of you who have taught, tolerated, scolded, encouraged, discouraged, challenged and befriended me, let me state it simply: thank you for enriching my life.

I now see the dangers inherent in making a list of names, but have decided to risk it on the grounds that I wish to express my indebtedness to some people publicly. I am grateful to William Martin and Andrew Galambos who literally opened up a new world of scientific thinking to my teenage mind, and life has never been the same. I am also grateful to Solomon Deressa, Chuck Campbell and Anders Carlsson, all of whom gave me a chance when I probably didn't deserve one, and from whom, I have learned much. It is a pleasure to acknowledge my various friends at Brown from whom I have taken the vast majority of the courses offered in our Solid Mechanics curriculum (B. Freund - Stress Waves, Thin Films; R. Clifton - Advanced Continuum Mechanics; K.-S. Kim - Foundations of Continuum Mechanics; A. Bower - Plasticity; F. Shih - Finite Element Method; C. Briant - Mechanical Properties of Materials; and Mig Ortiz who taught Dislocations in Solids and much else through private consultation). Indeed, the inimitable Professor Ortiz has been the kind of friend and collaborator that one is lucky to find even once. My good fortune at Brown has also been built around the chance to learn from a series of outstanding graduate students and postdocs. Ellad Tadmor, Ron Miller, Vijay Shenoy, David Rodney and Harley Johnson all were a key part of my first five years at Brown and I can only hope they learned a fraction as much from me as I did from them. More recently, I have benefited enormously from my interactions with Nitin Bhate, Dan Pawaskar, Kedar Hardikar and David Olmsted.

As I said above, much of the fun in writing this book came from the interactions I had with others. I must single out Kaushik Bhattacharya, Rick James, Art Voter, Mig Ortiz, Chris Wolverton, Vivek Shenoy and Mark Asta, all of whom need special acknowledgement for running a veritable intellectual babysitting operation. I have also benefited from expert advice on a number of different chapters from Janet Blume, Jane Kondev, Craig Black, Saryn Goldberg, Deepa Bhate, Anders Carlsson, K.-J. Cho, John Jameson, Tim Kaxiras, Stephen Foiles, Fabrizio Cleri, Mark Asta, Chris Wolverton, Art Voter, Luciano Colombo, Ladislas Kubin, Lyle Roelofs, Lloyd Whitman, Clyde Briant, Ben Freund, Dan Pawaskar, Karsten Jacobsen, Perry Leo, Kaushik Bhattacharya, Rick James, Simon Gill, Kevin Hane, T. Abinandanan, Peter Gumbsch, Long-Qing Chen, Georges Saada, Peter Voorhees, Alan Ardell, Emily Carter, Alan Needleman, Sam Andrews, Didier de Fontaine, Jakob Schiotz, Craig Carter, Jim Warren, Humphrey Maris, Zhigang Suo, Alan Cocks, Gilles Canova, Fred Kocks, Jim Sethna, Walt Drugan, Mike Marder, Bob Kohn, and Bill Nix and Mike Ashby indirectly as a result of a series of bootlegged course notes from excellent courses they have given. My book has also been read cover to cover by a number of hearty souls (Ron Miller, David Rodney, David Olmsted, Rob Rudd, Nitin Bhate, Walt Drugan and Bill Curtin) who made immensely useful suggestions that took my manuscript from an infantile performance to something that might be considered presentable. Of course, any errors that remain are strictly my own responsibility and indeed, at several junctures throughout the text, my arguments are suspect. It is also my great pleasure to thank Maryam Saleh who literally sketched, traced, drew and redrew over 300 figures, and Lorayn Palumbo who took care of everything from making sure I didn't forget to teach my class to taking care of all manner of miscellaneous tasks. I am happy to extend my warmest thanks also to Amy Phillips who submitted literally hundreds of requests for permission to reprint figures. I would also like to thank Florence Padgett from Cambridge University Press who has supported me through the various stages of frustration that attended the writing of this book and, similarly, Simon Capelin. I would also like to acknowledge the outstanding editorial efforts of Maureen Storey who suggested all manner of improvements. The opportunity to write this book was supported generously through my wonderful NSF Career Award.

As will be evident to any reader of my book, I have tried to present as many of my conclusions as possible in pictorial form. The task of amassing the various figures that form the backbone of this work was lightened enormously by the generous help of many friends, namely, Sharvan Kumar, Mike Mills, Peter Voorhees, Dan Fridline, Allan Bower, Alan Schwartzman, Harley Johnson, Karsten Jacobsen, Jakob Schiøtz, Rolf Heid, Rajiv Kalia, Sanjay Kodiyalam, Rick James, Kedar Hardikar, Dan Pawaskar, Charles McMahon, Vasily Bulatov, David Vanderbilt, Ralf Mueller, Lindsey Munro, Luciano Colombo, Tomas de la Rubia, George Gilmer, Christophe Coupeau, Marc Legros, Kevin Hemker, Sean Ling, Ian Robertson, Torben Rasmussen, Nasr Ghoniem, Klaus Schwarz, Marc Fivel, Bill Gerberich, David Rodney, Vivek Shenoy, Hans Skriver, Lloyd Whitman, Furio Ercolessi, Martin Bazant, Dieter Wolf, David Seidman, Craig Carter, Eric Chason, Stuart Wright, Brent Adams, Bob Hyland, Subra Suresh, Clyde Briant, Alan Ardell, Mitch Luskin, Liz Holm, Simon Gill, T. Abinandanan, Long Chen, Michael Ortiz (da Mig), Eberhard Bodenschatz, Art Voter, Chris Roland, Chris Wolverton, Charles-Andre Gandin, Michel Rappaz, Nik Provatas, John Hamilton, Farid Abraham, Harry Bhadesia and David Clarke. Thank you all again.

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### Notes on Units, Scales and Conventions

In the chapters to follow, one of our aims is to try to recast many of our results in numerical form, giving an impression of the many interesting scales (length, time, energy, stress, etc.) that arise in discussing solids. A prerequisite to such discussions is to make sure that a correspondence has been constructed between the units favored here and those encountered in the everyday experience of the reader.

Geometric and Structural Notions. One of the most significant single ideas that will appear in what follows is the important role played by geometric structures at a number of different scales within materials. Indeed, the coupling between structure and properties is an element of central orthodoxy in materials science. In characterizing the structures within materials, it is clearly overly pedantic to hold to any single set of units for characterizing such structures, and we will comfortably interchange between a few different units of measure. The smallest scales that we will touch upon are those tied to the existence of atoms and their arrangements to form crystalline solids. Two fundamental units of length are most popular in this setting, namely, the ångstrom (1 Å =  $10^{-10}$  m) and the Bohr radius ( $a_0 \approx 0.529\,177 \times 10^{-10}$  m). The ångstrom should be seen as a member in the series of scales which are all simple factors of 10 away from the meter itself. On the other hand, the Bohr radius arises as a natural unit of length in assessing atomic-scale processes since it is built up as a combination of the fundamental constants characterizing these processes, namely,  $a_0 = \hbar^2 / m_e e^2$ , where  $\hbar$  is Planck's constant,  $m_e$  is the mass of the electron and e is the charge on an electron.

We will also occasionally resort to the use of nanometers  $(1 \text{ nm} = 10^{-9} \text{ m})$  as an alternative unit of length when characterizing atomic-scale processes. When characterizing structures at the microstructural level, we will try to hold to a single unit of length, the micron  $(1 \mu \text{m} = 10^{-6} \text{ m})$ . Note that a human hair has dimensions on the order of 50 µm. The use of both nanometers and microns will be seen as characteristic of the dimensions of many structural features such as precipitates and inclusions as well as the grains making up polycrystals. In our ambition of providing meaningful geometric classifications of solids, it will also be necessary to make reference to units of area and volume, both of which will be reported either using ångstroms or meters as the base unit, resulting in either  $Å^2$  or  $m^2$  for areas and  $Å^3$  or  $m^3$  for volumes.

**Time Scales and Temporal Processes.** One of our recurring themes in the pages to follow will be the role of disparate scales in characterizing processes and structures within materials. In addition to the diversity of spatial scales, there are a host of processes in solids which are themselves characterized by widely different time scales. As a result, we will be forced to adopt a series of different measures of the passage of time. One of the elemental processes in solids that will occupy much of our attention is that of the vibrations of solids. As will become evident in later chapters, atomic vibrations are characterized by frequencies on the order of  $10^{13}-10^{14}$  Hz, which corresponds to a time scale on the order of one-tenth of a picosecond. As a result, we will make use of both 1.0 fs =  $10^{-15}$  s and 1.0 ps =  $10^{-12}$  s in describing atomic motions.

Force and Energy. Just as with the characterization of the various geometric structures that populate solids we will stick to a few standard units of measure: we will adopt a strategy of characterizing the various measures of force, stress and energy in terms of a few basic units. The two units of force that will occupy centerstage in the pages that follow are the standard MKS unit, the newton, and the less familiar choice of eV/Å (eV is a unit of energy) which is much more representative of the types of forces that arise in characterizing atomic-scale motions. When translated into units of stress, we will find it advantageous again to adopt two distinct sets of units, namely, the MKS unit of stress, the pascal  $(1 \text{ Pa} = 1 \text{ N/m}^2)$  and the atomic-scale analog,  $eV/Å^3$ . In addition, we will find it convenient to interchange between units of energy reported in both joules and electron volts (eV). In particular, we recall that the conversion between these two sets of units is given by  $1.0 \text{ eV} \approx 1.602 \times 10^{-19} \text{ J}$ . On the other hand, from time to time we will also invoke the rydberg as a unit of energy. This unit of energy arises naturally in characterizing the energy levels of atoms and can be expressed in terms of fundamental constants as  $Ry = me^4/2\hbar^2$ . Note that the conversion between Ry and eV is, 1 Ry = 13.6058 eV. In our analysis of activated processes, we will repeatedly find it advantageous to reckon our energies in dimensionless form, where the energy scale is determined by  $k_B T$ , here  $k_B \approx 1.38 \times 10^{-23} \text{ J/K}$ is Boltzmann's constant. We note that a useful rule of thumb is that for room temperature,  $k_B T \approx 1/40$  eV. For the remainder of the book, we will suppress the subscript on  $k_B$ .

**Material Parameters.** The key means whereby material specificity enters continuum theories is via phenomenological material parameters. For example, in describing the elastic properties of solids, linear elastic models of material response posit a linear relation between stress and strain. The coefficient of proportionality is the elastic modulus tensor. Similarly, in the context of dissipative processes such as mass and thermal transport, there are coefficients that relate fluxes to their associated driving forces. From the standpoint of the sets of units to be used to describe the various material parameters that characterize solids, our aim is to make use of one of two sets of units, either the traditional MKS units or those in which the eV is the unit of energy and the ångstrom is the unit of length.

**Conventions.** During the course of this work we will resort to several key conventions repeatedly. One important example is that of the summation convention which instructs us to sum on all repeated indices. For example, the dot product of two vectors may be written

$$\mathbf{a} \cdot \mathbf{b} = a_1 b_1 + a_2 b_2 + a_3 b_3 = a_i b_i. \tag{1}$$

A second key notational convention that will be invoked repeatedly is the definition of the dyadic product given by  $(\mathbf{a} \otimes \mathbf{b})\mathbf{v} = \mathbf{a}(\mathbf{b} \cdot \mathbf{v})$ . Another key convention that will be used repeatedly is the notation that  $\{a_i\}$  refers to the set  $a_1, a_2, \ldots, a_N$ . When carrying out integrations, volumes will typically be denoted by  $\Omega$  while the boundary of such a volume will be denoted as  $\partial \Omega$ .

# Part one

## Thinking About the Material World

## Idealizing Material Response

#### 1.1 A Material World

Steel glows while being processed, aluminum does not. Red lasers are commonplace, while at the time of this writing, the drive to attain bright blue light is being hotly contested with the advent of a new generation of nitride materials. Whether we consider the metal and concrete structures that fill our cities or the optical fibers that link them, materials form the very backdrop against which our technological world unfolds. What is more, ingenious materials have been a central part of our increasing technological and scientific sophistication from the moment man took up tools in hand, playing a role in historic periods spanning from the Bronze Age to the Information Age.

From the heterostructures that make possible the use of exotic electronic states in optoelectronic devices to the application of shape memory alloys as filters for blood clots, the inception of novel materials is a central part of modern invention. While in the nineteenth century, invention was acknowledged through the celebrity of inventors like Nikola Tesla, it has become such a constant part of everyday life that inventors have been thrust into anonymity and we are faced daily with the temptation to forget to what incredible levels of advancement man's use of materials has been taken. Part of the challenge that attends these novel and sophisticated uses of materials is that of constructing reliable insights into the origins of the properties that make them attractive. The aim of the present chapter is to examine the intellectual constructs that have been put forth to characterize material response, and to take a first look at the types of models that have been advanced to explain this response.

#### 1.1.1 Materials: A Databook Perspective

What is a material? The answer to this seemingly nonsensical question strikes right to the heart of some of the key issues it is the aim of this book to examine.

From the most naive of perspectives, questions surrounding the defining qualities of a particular material are easily answered in terms of our everyday perceptions: weight, luster, color, hardness, susceptibility to heating. However, these simple notions are a reflection of a deeper underlying identity, an identity that is revealed quantitatively the moment one poses the question of precisely how a given material replies when affected by some external probe. If we subject a material to a force, it changes shape. If we apply a potential difference, electrical current might flow. And if the temperatures of the two ends of a sample are different, a flow of heat results. In each of these cases, these experiments reveal something further about the identity of the material in question.

One of the overarching conceptual themes that has emerged from such simple experiments and that rests behind the quantitative description of materials is the idea of a material parameter. For example, Hooke's original efforts, which were aimed at uncovering the relation between a body's extension and the applied force that engendered it, led to the recognition that there exist a series of numbers, namely the elastic moduli, that characterize the elastic response of that material under different loading conditions. Similarly, there is a well established tradition of subjecting materials to applied fields which result in the emergence of various fluxes such as the electrical and thermal currents mentioned above. Allied with these fluxes are material parameters that link the response (i.e. the flux) to the applied field. In these cases and many more, the central idea is that a particular material can be identified in terms of the specific values adopted by its material parameters. In fact, for some purposes, a particular material may be idealized completely in terms of a set of such parameters. For the elastician, single crystal Al is characterized by a density and three elastic constants, namely,  $C_{11}$  = 106.78 GPa,  $C_{12} = 60.74$  GPa and  $C_{44} = 28.21$  GPa (data for Al at 300 K taken from Simmons and Wang (1971)). By way of contrast, to the engineer concerned with the application of Al in thermal environments, Al is specified in terms of a density and a thermal conductivity  $\kappa = 2.37$  W/(cm K) (data for Al at 300 K taken from Shackelford et al. (1995)). This type of idealization of a material in which its entire identity is represented by but a few numbers is one of far-reaching subtlety. In the context of the elastic constants, all of the relevant atomic bond stretching and bending has been subsumed into the three material parameters introduced above. Similarly, the full complexity of the scattering of phonons giving rise to the thermal properties of a material has also been subsumed into just one or a few numbers. One of our primary missions in the coming chapters will be to explore how such effective theories of material behavior may be built strictly on the basis of such material parameters and to examine what gives rise to the difference in these parameters from one material to the next.

From the standpoint of the idea given above, a particular material is characterized by a set of numbers that can be unearthed in a databook. For example, important parameters include the density  $\rho$ , the yield stress  $\sigma_{v}$ , the fracture toughness  $K_{IC}$  and the diffusion constant D. We note that in each case there is a number that can be looked up that characterizes the weight of a material in some normalized terms (i.e. the density), the resistance of the material to permanent deformation and fracture (yield strength and toughness), the ease with which mass can be transported within the material at elevated temperatures (diffusion constant) and any of a number of other possibilities. Our main point is to illustrate the way in which a given number (or set of numbers) can be used to introduce material specificity into continuum treatments of material response. For example, in considering the continuum treatment of mass transport, it is held that the flux of mass is proportional to the gradient in concentration, with the constant of proportionality being the diffusion constant. This same basic strategy is exploited repeatedly and always hinges on the fact that the complexity of the atomic-level processes characterizing a given phenomenon can be replaced with a surrogate in the form of material parameters.

The significance of the notion of a material parameter is further clarified by putting the properties of different materials into juxtaposition with one another. In figs. 1.1 and 1.2, we follow Ashby (1989) with some representative examples of the range of values taken on by a few prominent material properties, namely the Young's modulus, the yield strength, the fracture toughness and the thermal conductivity. The basic idea adopted in Ashby's approach is to allow the contrasts between the properties of different materials to speak for themselves. One of our aims in the chapters that follow will be to develop plausible explanations for the range of data indicated schematically in fig. 1.1, with special attention reserved for thermomechanical properties.

Despite the power of the idea of a material parameter, it must be greeted with caution. For many features of materials, certain 'properties' are not *intrinsic*. For example, both the yield strength and fracture toughness of a material depend upon its internal constitution. That is, the measured material response can depend upon microstructural features such as the grain size, the porosity, etc. Depending upon the extent to which the material has been subjected to prior working and annealing, these properties can vary considerably. Even a seemingly elementary property such as the density can depend significantly upon that material's life history. For a material such as tungsten which is often processed using the techniques of powder metallurgy, the density depends strongly upon the processing history. The significance of the types of observations given above is the realization that many material properties depend upon more than just the identity of the particular atomic constituents that make up that material. Indeed, one of our central themes will



Fig. 1.1. Elastic and plastic properties of a wide class of materials (adapted from Ashby (1989)).



Fig. 1.2. Fracture and thermal properties of a wide class of materials (adapted from Ashby (1989)).

be the argument that microstructural features such as point defects, dislocations and grain boundaries can each alter the measured macroscopic 'properties' of a material.

One of our primary concerns in the pages that follow is to understand the emergence of material properties on the basis of the geometric structures that populate materials. This critical link between structure and properties has been canonized through the structure–properties paradigm which elevates the analysis of structure as a prerequisite to understanding properties. We have tried, in this section, to present something of the backdrop against which we will develop models of material behavior, especially with reference to thermomechanical properties. As an introduction to such models we first examine the role played by geometric structure in dictating material properties, followed by an overview of the ways in which materials may be tailored to yield particular values of these material parameters.

#### 1.1.2 The Structure-Properties Paradigm

In the previous section we noted that, in the abstract, Al (or any other material) may be characterized by a series of numbers, its material parameters, to be found in a databook. However, as we already hinted at, because of the history dependence of material properties, the description of such properties is entirely more subtle. There is no one aluminum, nor one steel, nor one zirconia. Depending upon the thermomechanical history of a material, properties ranging from the yield strength to the thermal and electrical conductivity can be completely altered. The simplest explanation for this variability is the fact that different thermomechanical histories result in different internal structures.

A fundamental tenet of materials science hinted at in the discussion above is the structure–properties paradigm. The claim is that by virtue of a material's structure many of its associated properties are determined. Structure is an intrinsically geometric notion and one of the abiding themes in this book will be the constant reminder that it is structure on a variety of different length scales that gives rise to many of the well-known properties of materials. From the atomic-scale perspective we will constantly return to the implications of the fact that a material has a given crystal structure, whether it be for its role in dictating the properties of interfacial defects such as antiphase boundaries or the elastic anisotropy that must enter elasticity theory if the crystal symmetries are to be properly accounted for. Next, we will devote repeated attention to the lattice defects that disturb the uninterrupted monotony of the perfect crystal. Vacancies, interstitials, dislocations, stacking faults, grain boundaries and cracks will each claim centerstage in turn. At yet lower resolution, it is geometry at the microstructural scale that comes into relief and will occupy much of our attention. At each of these scales we will return to


Fig. 1.3. Yield strength data for steel as a function of grain size d (adapted from Leslie (1981)). Plot shows dependence of yield stress on inverse power of grain size. The legends at the top of the figure show the actual grain size as measured in both  $\mu$ m and using the ASTM units for grain size.

the question of the structure–properties paradigm, always with a critical eye, to see just how far it may take us in our desire to unearth the behavior of real materials.

A celebrated example of the coupling of structure and properties is exhibited in fig. 1.3 in which the relation between the yield strength and the grain size is depicted. In particular, the Hall–Petch relation posits a relation between the yield stress and the grain size of the form  $\sigma_y \propto 1/\sqrt{d}$ , where *d* is the grain size of the material. The Hall–Petch relation leads us to two of the most important notions to be found in contemplating materials: the existence of microstructure and its implications for material properties, and the development of scaling laws for characterizing material response. An immediate consequence of the results depicted here is the insight that not only are structures at the atomic scale important, but so too are the geometric structures found at the microstructural scale.

We have noted that the attempt to understand materials demands that we confront a hierarchy of geometric structures, starting with the atomic-level geometries presented by the crystal lattice and increasing in scale to the level of the isolated defects that exist within materials to their assembly into the material's microstructure itself. The quest to understand the structure of a given material inevitably commences with the phase diagram. Phase diagrams are one of the primary road maps of the materials scientist. Such diagrams represent a summary of a series of tedious analyses aimed at determining the *equilibrium* atomic-scale structure of a given element or mixture of elements for a series of temperatures (and possibly



Fig. 1.4. Phase diagram of elemental sulfur (adapted from Young (1991)).

pressures). In figs. 1.4 and 1.5, we show the equilibrium phase diagrams of elemental sulfur and the iron–carbon system. The particular choices of materials shown here are meant to give a feel for the existence of the rich atomic-level complexity that is found in both elemental systems and their alloy counterparts. Note that in the case of elemental sulfur, there are not less than ten different equilibrium structures corresponding to different values of the temperature and pressure. These structures are built around molecular S<sub>8</sub> and range from orthorhombic to monoclinic lattices. The iron–carbon phase diagram illustrates a similar structural diversity, with each phase boundary separating distinct structural outcomes.

Phase diagrams like those discussed above have as their primary mission a succinct description of the *atomic-level* geometries that are adopted by a given system. However, as we have already mentioned, there is structure to be found on many different length scales, and one of the surprises of deeper reflection is the realization that despite the fact that phase diagrams reflect the equilibrium state of a given material, they can even instruct us concerning the *metastable* microstructures that occur at larger scales. The simplest example of such thinking is that associated with precipitation reactions in which an overabundance of substitutional impurities is frozen into a system by quenching from high temperatures. If the material is subsequently annealed, the phase diagram leads us to expect a two-phase



Fig. 1.5. Phase diagram for the iron-carbon system (adapted from Ashby and Jones (1986)).

microstructure in which the overabundance of substitutional impurities is now taken up in the relevant equilibrium phase. What this suggests is that strategies can be concocted for preparing particular metastable states with desirable properties. It is this insight that has led to many of the heat and beat strategies that have attracted pejorative attention to the materials engineer. A broad description of the significance of phase diagrams to materials science may be found in Massalski (1989).

As noted above, the phase diagram instructs our intuitions concerning the atomic-level geometries of materials. At the next level of geometric complexity in the hierarchy of structures that exist within a material, we must confront the defects that populate materials. Indeed, one of the key realizations that we will revisit from a number of different perspectives is that of the role of defects in the determination of material response. What this means is that the structure–properties paradigm makes an ambiguous use of the word 'structure' since in different situations, the structures being referenced can range all the way from atomic-scale structure to that of the nature of the grains making up a polycrystal. At the level of the defect

geometries found within materials, our present argument is that if we trace yield in crystals to the mechanisms which engender it for example, it is the motion of dislocations which will be implicated. Similarly, if we pursue the stress–strain curve to its limits, the material will fail either through crack propagation or void coalescence or some other defect mechanism. The implication of this insight is that much of the work of modeling the thermomechanical behavior of materials can be reduced to that of carrying out the structure–properties linkage at the level of defect structures within materials.

In later chapters, we will adopt a hierarchical approach to constructing models of material response. First, we will examine the way in which atomistic models can be used to uncover the structural rearrangements in defect 'cores' which are a signature of the nonlinear interatomic interactions that are difficult to capture within continuum theory. Once these tools are in hand, we will turn to an analysis of the dominant defect types themselves, with a classification scheme centered on the dimensionality of these defects. Having successfully captured the structure and energetics of single defects, our next mission will be to understand the role of defects as conspiratorial partners in the emergence of observed macroscopic behavior. The uncovering of this conspiracy will in the end always lead us to questions of averaging. The challenge here is in forging the connection between the behavior of single defects, on one hand, and the macroscopic material response, on the other, which often emerges as a synthetic response of many defects in concert.

## 1.1.3 Controlling Structure: The World of Heat and Beat

In the previous section we considered the critical role played by structures at a number of different scales in determining material properties. From the standpoint of the materials engineer this insight may be recast as a challenge: how may the various structures within a material be tailored so as to yield desired properties? Metallurgy has a longstanding reputation as an empirical subject founded upon the twin pillars of heating and beating a material to some desired form. Whether one resorts to cold working a material or subjecting it to a high-temperature anneal, the outcome of these *processes* is a change in the internal constitution of that material at one or more scales. Because of these structural changes, there is a concomitant change in the properties of the material. Indeed, these strategies for altering the structure of materials should be seen as the answer to the challenge posed above.

By carefully selecting the thermal and mechanical history of a material, it is possible to tailor a number of different features of that material. Low-temperature anneals can induce precipitate reactions that increase the yield stress. Cold working changes the dislocation density, and this too alters the yield stress. If the material



Fig. 1.6. Schematic of the different microstructures for the Ni–Al system that are obtained using different thermomechanical processing schedules (adapted from Kumar *et al.* (1992)). The figure illustrates precipitation at grain boundaries and within grains.

is exposed to a particular chemical atmosphere it can result in a thin surface layer that can increase the material's hardness, a strategy that is adopted in the production of carburized steels. In each of these examples, through annealing (heat) or deformation (beat) or both, the internal structures within the material are changed and as a result, so too are the macroscopic properties.

As an explicit example of how a material changes when subjected to the type of processing program introduced above, fig. 1.6 shows a schematic of the microstructures that arise from slightly different chemical compositions and for different thermal histories for Ni-rich Ni–Al alloys. The figure illustrates the significant variety in microstructure as a function both of slight (<3%) changes in chemical composition and in the aging process. As a result of the aging process, second-phase particles of either Ni<sub>3</sub>Al or Ni<sub>5</sub>Al<sub>3</sub> can develop. In addition, if the sample is initially slow cooled, Ni<sub>3</sub>Al precipitates at grain boundaries, while quenching and subsequent aging induces precipitation in the matrix. As is also indicated in the figure in the striped regions in the middle row, another microstructural outcome is the development of Ni–Al martensite. Out of the series of specimens indicated schematically in the figure, each of which had a different microstructure, the fracture toughnesses varied by as much as nearly a factor of

2. The role of this example in the current discussion is twofold: first, we wish to illustrate the significant structural differences that attend different processing schedules, and second, we aim to show the inextricable link between measured properties and structural features at the microstructural level.

The richness of the microstructures that result from different thermomechanical processing histories is perhaps best illustrated through the example of steels. As was indicated in fig. 1.5, at temperatures below roughly 720 °C, the equilibrium constitution of an Fe–C alloy in the low carbon concentration limit is a two-phase alloy consisting of both  $\alpha$ -Fe (ferrite, in the bcc structure) and Fe<sub>3</sub>C. However, this description merely tells us which crystal structures are present. The microstructure that attends the presence of these structures is known as pearlite and consists of alternating plates of  $\alpha$ -Fe and Fe<sub>3</sub>C. For the purposes of the present discussion we wish to note that there are a wide variety of metastable microstructures that can be attained which feature the different phases revealed in the phase diagram. For further details the reader is urged to consult Ashby and Jones (1986) or Honeycombe and Bhadeshia (1995).

In this first section of the book, our intention has been to illustrate the abstract representation of materials by different material parameters and to show how via the structure–properties linkage, material properties can be tuned by controlling the structures themselves. From a quantitative viewpoint, material response is characterized in terms of a series of material parameters that we have argued depend heavily on the internal constitution of materials at a number of different scales. These internal structures can be controlled by a number of different processing strategies. This series of insights now leaves us with the main substance of the type of questions that must be tackled in constructing viable models of material response.

## 1.2 Modeling of Materials

## 1.2.1 The Case for Modeling

Modeling has quietly become a ubiquitous part of daily life. Each evening's weather forecast leans heavily on the existence of well-defined theoretical models that are built around the vast quantities of data that are recorded at worldwide weather stations each day. Wall Street thrives on the existence of financial derivatives based largely on stochastic models of pricing and value. In the manufacturing arena, the release of the Boeing 777 exemplifies a reliance on modeling heretofore unknown: structural mechanics and aerodynamics, flight dynamics, operations research, process modeling, modeling of manufacturing, all were part of this huge project. Modeling has assumed an increasingly important role in the materials context as well.

The role of modeling in the materials setting is quite diverse. On the one hand, in the design process, the uses to which materials will be put must be evaluated critically with an eye to performance, reliability and safety. In addition, modeling can play a role in the quest to control materials and the processes used to produce them. At the most fundamental level (and the primary focus of the present work), modeling serves as the basis for an understanding of materials and their response to external stimuli. Broadly speaking, the demands placed on a model strongly depend upon its intended use. Bronze Age practitioners were successful in their material choices without detailed understanding. The challenge of modern alloy design, by way of contrast, is to see if the quantitative understanding from the modern theory of defects may be used to suggest new material strategies. On the one hand, phenomenological models may be entirely satisfactory if the goal is to test the response of a given material to casting in different shapes, for example. On the other hand, if the goal is to produce mechanistic understanding with allied predictive power a phenomenological model may not suffice and might be replaced by detailed insights concerning the underlying mechanisms. From the perspective of the engineer, the pinnacle of the modeling approach is the ability to alter engineering strategies through either the design of new materials or the institution of new processes for exploiting existing materials.

From the perspective of understanding why materials are the way they are, two of the most compelling examples that can be given concern the deformation and ultimate failure of solids. Though we will take up both of these issues again later from a quantitative perspective, our present aim is to illustrate the conceptual leap in understanding that attended the solution to the puzzles of plastic deformation and fracture. The simplest models of both of these processes consider homogeneous solids. In the case of plasticity, deformation was first posited to result from the uniform sliding of adjacent crystal planes, while fracture was envisaged to arise from a similar homogeneous process in which adjacent planes are uniformly separated. The problem with these simple models is that they lead to critical stresses for these processes that are well in excess of those observed experimentally. In both cases, the resolution of the paradox came from modeling insights concerning the role of defects in reducing the critical stresses for these processes. In the case of plastic deformation, the introduction of the dislocation resolved the discrepancy, while in the case of fracture, it was the presumed presence of preexisting cracks.

#### **1.2.2 Modeling Defined: Contrasting Perspectives**

As is perhaps already evident, the idea conveyed by the word 'modeling' is ambiguous. This ambiguity is ultimately linked to fundamental questions concerning the aims of science itself. At the most fundamental level, there is an age old debate concerning the true object of science: are we describing some underlying reality in nature, or rather is the aim to elucidate rules that yield successively better approximations to what we observe in the world around us? From the latter perspective, even the elaboration of Maxwell's equations or the edifice of classical thermodynamics might be seen as profound exercises in modeling. These types of advances must be contrasted with those in which it is clear from the outset that what is being done is picking off some fundamental feature of what has been observed and casting it in mathematically tractable terms with the aim of making falsifiable predictions.

These arguments are perhaps best illustrated by recourse to examples which serve to demonstrate the ways in which fundamental laws must be supplemented by models of material response. Whether we discuss the electromagnetically busy vacuum of interplanetary space, the absorption of radiation by an insulator or the ceramic innards of a capacitor, our expectation is that Maxwell's equations are the appropriate theoretical description of the underlying electromagnetic response. This part of the 'modeling' process was finished in the last century. On the other hand, the description in terms of these equations alone is incomplete and must be supplemented by constitutive insights which provide a description of the electromagnetic *properties* of the medium itself. In this context we refer to quantities such as the dielectric constant and the magnetic susceptibility. For example, with reference to optical absorption, the classical model of Lorentz assumed that the charges within a material could be thought of as tiny harmonic oscillators with a particular natural frequency. The electromagnetic field impinging on the material has the effect of forcing these oscillators, with the result that one can determine the absorption as a function of incident frequency. Note the character of this model. It is noncommittal with respect to any fundamental description of the material. Rather, it aims to reflect some element of the reality of the material in a way that can be calculated and compared with experiment, and, if successful, used as the basis of design.

As another example, this time drawn from the realm of classical thermodynamics, we may consider the thermal state of a neutron star, a high-temperature superconductor or a dense gas. In each case, there is little doubt as to the validity of thermodynamics itself. On the other hand, if we wish to make progress in the description of the dense gas, for example, the laws of thermodynamics by themselves do not suffice. This is where modeling in the sense that it will be used primarily in this book comes in. In addition to the fundamental laws that apply to *all* thermodynamic systems, we must characterize those features of the problem that are nonuniversal. That is, we require an equation of state which has nowhere near the same level of generality as the laws of thermodynamics themselves. Again, one turns to models whose aim is a characterization of the properties of matter. Different gases in different density regimes are appropriately described by different equations of state.

These examples, and others like them, allow us to discern three distinct levels of model building, though admittedly the boundary between them is blurred. In particular, the level of such modeling might be divided into (i) *fundamental laws*, (ii) *effective theories* and (iii) *constitutive models*. Our use of the term 'fundamental laws' is meant to include foundational notions such as Maxwell's equations and the laws of thermodynamics, laws thought to have validity independent of which system they are applied to. As will be seen in coming paragraphs, the notion of an 'effective theory' is more subtle, but is exemplified by ideas like elasticity theory and hydrodynamics. We have reserved 'constitutive model' as a term to refer to material-dependent models which capture some important features of observed material response.

To make the distinction between effective theories and constitutive models more clear, we consider both elastic and hydrodynamic theories in more detail. The existence of elasticity theories is an example of what we mean by an effective theory. The central thrust of such theories is that some subset (or linear combination or average) of the full microscopic set of degrees of freedom is identified as sufficing to characterize that system, or alternatively, the system is described in terms of some new phenomenological degrees of freedom (i.e. an order Indeed, one of the threads of recent scientific endeavor is the contention that reductionistic dogma is unfit to describe *emergent* properties in which it is the synthetic properties of the many-particle problem itself that yield many of the fascinating phenomena of current interest. Generally, we do not undertake a structural analysis of the Golden Gate Bridge or the beautiful convective patterns seen in the clouds from an airplane window on an atom by atom basis. These examples lead more naturally to effective descriptions in which one imagines the identification of an order parameter that characterizes the emergent property, and for which there is some appropriate continuum description.

Once the degrees of freedom have been identified, a dynamics of these degrees of freedom is constructed. To continue with our elaboration of the sense in which both elasticity and hydrodynamic theories serve as paradigmatic examples of such thinking, we note that in the case of elasticity (we have yet to say precisely which elastic *constitutive* model we have in mind) the characterization of the system is in terms of kinematic quantities such as displacements and strains which are themselves surrogates for the full atomic-level description of the system. Similarly, in the hydrodynamic context, velocities and strain rates replace an atom by atom description of the system. What all of these examples have in common is their reliance on a truncated description of material response in which the underlying

discrete nature of the material is abandoned and is replaced by an effective theory in which microscopic processes have been subsumed into material parameters.

A key feature of the types of effective theories introduced above is that they depend upon the existence of a set of parameters that the theory itself is unable to determine. The elastic modulus tensor arises in describing linear elastic materials and the viscosity serves to characterize the hydrodynamic response of fluids. Similarly, the thermal conductivity arises in contemplating continuum models of heat conduction, while the magnetic susceptibility and the dielectric constant (to name a few) reflect a material's response to electromagnetic fields. What we learn from this observation is that normally effective theories like those described above must be tied to constitutive models which serve to distinguish one material from the next. Hence, we see that in addition to the level of modeling that is done in constructing the effective theory in the first place, there is a second key step in the modeling process in which *material specificity* is introduced. The elaboration of these various levels of modeling is one of the primary missions of the remainder of the book.

## 1.2.3 Case Studies in Modeling

One subbranch of materials science that has especially benefited from cross fertilization from different fields is that of the mechanical behavior of materials, itself one of the primary thrusts of the modeling efforts to be described in this book. The traditional disciplines of mechanical and civil engineering draw from the repository of information concerning the behavior of structural materials under both thermal and mechanical loading, with resulting structures from the Eiffel Tower to spacecraft that carry out 'fly-by' missions to distant planets. At more human size scales such as in the use of materials in applications ranging from lubricants on magnetic recording disks to the tungsten filaments that light millions of homes each evening, the interface between chemistry, materials science and condensed matter physics is obvious. Some of the issues that arise in the treatment of problems like these are the role of chemical impurities in either hardening materials or weakening grain boundaries, the ways in which microstructural size and shape influence both yield strength and ultimate resistance to fracture and the dazzling number of processing steps that attend the development of key technologies such as the Pentium chip which presides over the computer on which I am writing these words. Our discussion thus far has emphasized the mechanics of constructing models of material response without illustrating the outcome of using them. In the present section, our aim is to show in qualitative terms the different sorts of models that might be set forth for modeling materials and what is learned from them.

**Modeling Phase Diagrams.** Earlier we noted that phase diagrams form one of the main backbones of materials science and are a fertile setting within which to pose many of the most interesting questions about materials. Dirac argued that once the Schrödinger equation was in hand, the rest of chemistry was just a matter of implementing sufficiently powerful numerical schemes for solving the relevant governing equations. To be exact, he noted in 1929:

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

Indeed, Dirac could have extended the scope of his claim to many problems in the study of materials, including phase diagrams, as problems in which the underlying governing equations are known, but which are at the same time characterized by oppressive complexity. On the other hand, an alternative argument can be made in that much of the most interesting physics present in treating problems with a high level of complexity such as phase diagrams is exactly that which we learn from trying to *avoid* the brute force calculation hinted at in Dirac's assertion. In particular, the physics of effective theory construction is precisely the business of replacing the brute force solution of the governing equations with some simpler description. Indeed, to enliven the discussion with dueling quotes we note that P. W. Anderson (1972) has remarked on this hierarchy of theories as follows:

But this hierarchy does not imply that science X is 'just applied Y'. At each stage entirely new laws, concepts, and generalizations are necessary, requiring inspiration and creativity to just as great a degree as in the previous one. Psychology is not applied biology, nor is biology applied chemistry.

To which we might add that modeling complex many degree of freedom systems is not just an application of what is already known about single degree of freedom systems. To my mind, one of the most exciting current activities in the physical sciences is precisely this self-conscious attempt to systematically eliminate degrees of freedom so as to construct theories demanding minimal information.

In chap. 6, we will take up the subject of phase diagrams, with special attention being given to the computation of such diagrams on the basis of atomic-level insights. One of the insights that will become evident when we delve into these questions more deeply is the large extent to which computing phase diagrams represents the confluence of ideas and methods from many distinct sources. On the one hand, these calculations demand the total energies of all of the imagined



Fig. 1.7. Phase diagram for oxygen ordering in the YBCO class of high-temperature superconductors (after Ceder (1994)).

structural competitors which is the playing out of solving the Schrödinger equation referred to above. The calculation of such energies will be one of the centerpieces in the chapters to follow. In addition, once these energies are obtained, they must be supplemented by statistical arguments for assessing the entropy associated with both configurational disorder and the presence of thermal vibrations. It will be seen that in some instances it is possible to use an effective Ising representation of the various structural competitors to replace the laborious case by case search over different structural competitors.

An example of the computed and measured phase diagrams for oxygen ordering in the Cu–O high-temperature superconductors is given in fig. 1.7. The basic idea is the construction of an effective description of the energetics of the various structural competitors and to rank order these competitors as a function of some control parameters such as the composition and the temperature. For each point in parameter space, the victor in this competition is the equilibrium structure. We will come back later to some of the explicit details involved in computing the phase diagram of fig. 1.7 and note for the time being only that the calculation of such phase diagrams is a key part of computational materials science.

Modeling Material Parameters. In section 1.1.1, we argued that in many instances an extremely powerful idea is that of a material parameter. Whether discussing elasticity, heat conduction, mass transport or magnetism, we can capture the particulars of a given material in terms of such parameters. As already alluded to, the continuum models of heat conduction or mass transport cannot instruct us as to why the values of transport coefficients in some materials are large while in others they are small. Consequently, an important mission in the attempt to figure out what makes materials tick is the ambition of deducing material parameters on the basis of microscopic models.

As a first reflection on calculations of this type, fig. 1.8 shows examples of the correspondence between macroscopic material parameters and a subset of the associated microscopic calculations that might be used to determine them. One example of the use of microscopic calculations to inform higher-level models concerning material parameters is that of the diffusion constant. One of the challenges posed by data on diffusion is its strong variability in the presence of 'short-circuit' diffusion pathways such as surfaces, grain boundaries and dislocations. From a microscopic perspective, the essential idea is to examine the energetics of the diffusing particle as it passes the saddle point connecting two different wells in the energy landscape. In this case, a conjecture is made concerning the dominant reaction pathway in terms of a reaction coordinate which provides a measure of the extent to which the system has passed from one state to the next. The energy at the saddle point is used to determine the activation energy for diffusion. This activation energy, in conjunction with a model of the frequency with which the diffusing species attempts to cross the barrier leads to the diffusion constant itself. The key point made in fig. 1.8 is the idea that the atomic-level calculations can be used to inform our understanding of a higher-level material parameter.

A second example revealed in fig. 1.8(c) and (d) is that of the thermal conductivity. The left hand frame shows the phonon dispersion relation for Ge (a subject we will return to again in chap. 5) as computed using microscopic analysis. The right hand frame shows the measured thermal conductivity itself. Without entering into details, we note that on the basis of a knowledge of both the phonon dispersion relation and the anharmonic coupling between these phonons, it is possible to build up an analysis of the thermal conductivity, again revealing the strategy of using microscopic calculations to inform our understanding of higher-level continuum quantities. These case studies are meant to exemplify the logical connection between microscopic calculations and material parameters. Much of the business of coming chapters will surround the details of such calculations.

**Modeling Dislocation Cores.** In an earlier section, we belabored the critical coupling of structure and properties, and this is another arena within which modeling can produce valuable insights. One of our insights concerning the importance of structure was that of the role of lattice defects in governing many



Fig. 1.8. Schematic illustration of the ways in which microscopic calculations may be exploited to model macroscopic material properties. The first example (frames (a) and (b)) illustrates the use of microscopic calculations to examine surface diffusion, while the second example (frames (c) and (d)) illustrates the analysis of phonons in Ge as the basis of an analysis of thermal conductivity. Figures adapted from (a) Kaxiras and Erlebacher (1994), (b) Gjostein (1972), (c) and (d) Omini and Sparavigna (1997).

of the properties of materials. There exists a mature elastic theory of such defects. However, this theory is plagued by the existence of singularities which preclude its use in the immediate vicinity of the dislocation itself. For understanding of the dislocation core region one must turn instead to insights from atomic-scale calculations. As an example of the types of successes that have been achieved in this vein, we consider the core structure for the Lomer dislocation in Al in fig. 1.9. In this instance, an embedded-atom model for the interactions between Al atoms was invoked in order to compute the forces between atoms which were then used in turn to find the energy minimizing dislocation core structure. As will be discussed



Fig. 1.9. Dislocation core in Al as seen experimentally using high-resolution transmission electron microscopy (a) and image simulation of results of atomistic simulation using embedded-atom potentials (b) (adapted from Mills *et al.* (1994)).

in due time, the significance of simulations like this is that they may even afford the opportunity to draw conclusions about the macroscopic plastic behavior of a material. In the present context, we merely note that atomic-level calculations of the atomic positions within the dislocation core are susceptible to comparison with positions deduced from high-resolution microscopy. Once confidence in the atomic-level structure has been attained, then one can begin the harder work of trying to uncover the implications of this structure for observed properties.

**Modeling Microstructure and its Evolution.** Until this point, we have emphasized the virtues of modeling efforts built from the smallest scales up. However, as we have already noted, in many instances it is preferable to construct our theoretical vision on the basis of continuum models. We have already made reference to the critical role of microstructure in determining material properties and it is in this arena that we will consider a case study in continuum modeling. In particular, we consider the problem of a two-phase microstructure in which second-phase particles are dispersed through a matrix and the question under consideration concerns the temporal evolution of this microstructure. In particular, the modeler can ask questions both about the temporal history of particle size and shape as well as about its privileged terminal shape.

The continuum basis of models of this type of microstructural evolution really amounts to a consideration of the competition between surface and elastic energies. Both the elastic and interfacial energies depend upon the shape and size of the second-phase particles, and may even depend upon the relative positions of



Fig. 1.10. Temporal evolution of a circular particle as a result of diffusive processes driven by the competing influences of interfacial and elastic energy. The parameter  $\tau$  is a dimensionless measure of the elapsed time (adapted from Voorhees *et al.* (1992)).

different particles which are linked to particle–particle interactions. It is argued that a given particle can change both its size and shape in time as a result of diffusive processes that transport mass from one particle to another, or from one part of a given particle to another. An example of the temporal evolution of an initially circular particle as a function of time is shown in fig. 1.10. The calculations leading to this figure are based upon a treatment of the coupled problem of solving the equations of mechanical equilibrium in conjunction with a treatment of mass transport. One of the aims of coming chapters will be to set up enough machinery concerning elastic and interfacial energies as well as diffusive processes so that we can delve more deeply into the theoretical structure that makes these calculations possible.

As was shown above, the modeling of observed phenomenology concerning the properties of materials need not necessarily adopt an atomistic perspective. In addition to the microstructural evolution associated with both shape changes and coarsening of two-phase microstructures, one can also imagine the evolution of microstructures under conditions in which the driving force for structural change is more palpable. In particular, electromigration is a problem of abiding interest in the context of materials exploited in the microelectronics setting. In this case, mass transport is biased by the presence of a symmetry breaking charge flow which couples to the underlying microstructure. In fig. 1.11, a series of snapshots revealing the evolution of a void in the presence of an electric field are shown. The numerical engine used in these calculations is the finite element method.

In this section, we have attempted to give various snapshots of the modeling process, primarily with the aim of giving a sense both of what can be accomplished by recourse to modeling, and the different mindsets that attend different modeling paradigms. The work of coming chapters will largely concern the question of how to undertake problems like those sketched above from a systematic quantitative perspective.



Fig. 1.11. Void evolution under conditions of electromigration (adapted from Fridline and Bower (1999)).

#### 1.2.4 Modeling and the Computer: Numerical Analysis vs Simulation

Our spin thus far on the subject of modeling has been primarily complimentary. On the other hand, the advent of powerful computers as a tool for the evaluation of physical problems has not been universally beneficial. As we will describe presently, the establishment of computer-based models is attended by both conceptual and computational difficulties. It is true that the act of creating a numerical incarnation of a given theory requires an unambiguous statement of that theory itself. It is not possible to 'code up' a theory unless the mathematical statement of that theory can be clearly articulated. But these virtues are accompanied by vices as well. Because of the ease with which computational models may be advanced, the act of validation, both conceptual and logical, becomes increasingly uncertain.

In the context of materials science, there is an increasing desire to 'simulate' one's way to understanding. But the notion of simulation is far reaching. On the one hand, one might imagine the possibility of taking a well-defined partial differential equation, built in turn on the basis of well-known physical laws, which remains out of reach because it is not tractable analytically. In this instance, the appeal of numerical approaches is immediate and their power is indisputable. By way of contrast, there are a number of problems for which the proper physical laws have not yet been elucidated and often researchers are reduced to the act of formulating models based upon *ad hoc* assumptions of questionable validity. For example, in the context of the formation of dislocation patterns, it remains unclear whether techniques based upon minimization of some energy functional provide a proper theoretical context or whether a completely different strategy based upon reaction–diffusion equations, for example, is more suitable.

Another difficulty that attends the increasing use of computational models is that of pedagogy. The increasing reliance on simulation suggests that the problems of current interest are so complex that they defy description in proper analytic terms. If it emerges that this scenario is correct (which I expect it is not), then this raises serious questions concerning conventional notions of pedagogy. Here I refer to the difficulty of passing useful information from one generation of researchers to the next. As a teacher, I find it entirely unsatisfactory to tell a student 'it is so because computer simulation says it is so'. Such utterances do not normally constitute understanding. As a result, even in those cases where numerical analysis has been resorted to in order to solve well-posed problems based upon physically reasonable models, there is much yet to be done to learn how to incorporate these results into the canon of ideas that are passed from one generation of researchers to the next.

An additional intriguing challenge posed by computer models is that of handling large space and time scales. Historically, statistical mechanics has served as the workhorse for handling the many-body problem. However, the advent of powerful computers has opened the door to actually simulating huge numbers  $(10^{10})$  of particles without entering into a debate as to how the many-particle aspects of the problem are assembled to yield macroscopic observables. It is this question of *emergence*, how macroscopic behavior is built up from microscopic motions, that remains as one of the prominent challenges for modelers, and will serve as one of the philosophical cornerstones in the chapters to follow.

#### **1.3 Further Reading**

*Made to Measure* by Philip Ball, Princeton University Press, Princeton: New Jersey, 1997. This semipopular book examines some of the key materials that are making headlines at the time of this writing. I found the book both enjoyable and very enlightening.

*Designing the Molecular World* by Philip Ball, Princeton University Press, Princeton: New Jersey, 1994. This book places a more chemical emphasis on some of the materials of interest here, with special attention given to the molecular origins of various processes.

*Molecules* by P. W. Atkins, W. H. Freeman and Company, New York: New York, 1987. Though the emphasis here is on molecules rather than materials *per se*, Atkins does a fantastic job of connecting structure and function and illustrates the type of thinking that materials science should emulate in the quest to explicate this connection.

*Metals in the Service of Man* by A. Street and W. Alexander, Penguin Books, London: England, 1998. I find this book fun and interesting and full of useful insights for courses. Part of their humor is revealed in their *Dramatis Personae* where such 'Principals' as IRON – the most important metal, ALUMINIUM – the light metal, second in importance to iron, MAGNESIUM – the lightweight champion, TITANIUM – the strong middleweight, etc. are introduced.

*Engineering Materials* Vol. 1 (second edition: Butterworth-Heineman, Oxford: England, 1996) and *Engineering Materials* (Pergamon Press, Oxford: England, 1986) Vol. 2 by M. F. Ashby and D. R. H. Jones. These two books provide, at a very readable level, a broad description of the properties and uses of materials. I particularly enjoy these books because they dare to give an all-encompassing view of the role of materials in a variety of settings.

Introduction to Engineering Materials: The Bicycle and the Walkman by C. J. McMahon, Jr and C. D. Graham, Jr, 1994 (private publication, available from author: http://www.seas.upenn.edu/mse/fac/mcmahon.html). This book is a general introduction to many of the properties of materials illustrated through the medium of a few key examples, namely, the bicycle and the walkman. I always enjoy looking up new topics in this book.

*Strong Solids* by A. Kelly and N. H. McMillan, Clarendon Press, Oxford: England, 1986. This book provides a number of intriguing insights into the origins of many of the mechanical properties of solids.

*Atlas of Stress–Strain Curves* edited by H. W. Boyer, ASM International, Metals Park: Ohio, 1987. Given that our mission is dominated by the quest to understand mechanical properties, this book gives a sense of the variety of data to be encountered on the most immediate of mechanical tests. Indeed, to understand the subtlety of real stress–strain curves should be seen as one of our primary goals.

*Metals Handbook* edited by Taylor Lyman, American Society for Metals, Metals Park: Ohio, 1972. Volume 7 of this series is *Atlas of Microstructures of Industrial Alloys* and provides a series of fascinating pictures of microstructures in metals. Our reason for including it as the basis for further reading associated with this first chapter is that it gives a sense of the diversity the modeler must face, even within the limited domain of metallurgy.

*Understanding Materials Science* by Rolf E. Hummel, Springer-Verlag, New York: New York, 1998. I find this book particularly appealing in that Hummel has attempted to interweave technical insights into materials with a discussion of their historical uses.

*Materials Science and Engineering – An Introduction* by William D. Callister, Jr, John Wiley and Sons, New York: New York, 1994. I have included this selection as a well-known example of an undergraduate materials science textbook in which many of the phenomena of interest in the present setting are introduced.

'On the Engineering Properties of Materials' by M. F. Ashby, *Acta Metall.*, **37**, 1273 (1989). This article gives an overview of many of the most important thermal and mechanical properties of materials. The presentation of data is provocative

and the allied discussions are enlightening. This article is a personal favorite that I hand out in most of my classes.

*Physical Metallurgy* edited by R. W. Cahn, North Holland Publishing Company, Amsterdam: The Netherlands, 1965. Cahn's books are made up of a series of articles by leading experts in the field. Topics ranging from phase diagrams to fatigue are represented from a modern perspective and, though the emphasis is on metals, the ways of thinking about materials are more general. There is a more recent version of this excellent series.

*Statistical Mechanics of Elasticity* by J. H. Weiner, John Wiley & Sons, New York: New York, 1983. Weiner's book has a number of interesting and useful insights into the meeting point between continuum mechanics and microscopic theories.

*Computational Materials Science* by Dierk Raabe, Wiley-VCH, Weinheim: Germany, 1998. Raabe's book is included here as an example of the high level to which a discussion of modeling materials may be taken. Raabe covers many topics similar to those covered in this book, though the emphasis is often different.

*Thermophysical Properties of Materials* by G. Grimvall, North-Holland Publishing Company, Amsterdam: The Netherlands, 1986. Grimvall has written an outstanding book that is largely neglected. The idea is to make a concrete and quantitative attempt to use the knowledge of solid-state physics to understand the properties of real materials. This is one of my favorite books.

*Solid State Physics* by N. W. Ashcroft and N. D. Mermin, Saunders College, Philadelphia: Pennsylvania, 1976. My relationship with this fine book reminds me of Mark Twain's quip that as he passed from the age of 15 to 20 he couldn't believe how much his father had learned. Indeed, with each passing year I am amazed at how their book improves. Should the reader wish to see a clear statement of the body of solid-state physics as it stood fifteen years ago and as it is used in the present work, Ashcroft and Mermin is where I recommend he or she look.

## TWO

# **Continuum Mechanics Revisited**

## 2.1 Continuum Mechanics as an Effective Theory

Materials exhibit structural features at a number of different scales, all of which can alter their macroscopic response to external stimuli such as mechanical loads or the application of electromagnetic fields. One of the fundamental difficulties faced in the modeling of materials is how to extract those features of the problem that are really necessary, while at the same time attaining some tolerable level of simplification. Traditionally, one of the favored routes for effecting the reduction of problems to manageable proportions has been the use of continuum theories. Such theories smear out features at 'small' scales such as the discrete phenomena that are tied to the existence of atoms and replace the kinematic description of materials in terms of atomic positions with field variables. Adoption of these strategies leads to theories that can describe material behavior ranging from deformation of polycrystals to mass transport to the behavior of domain walls in magnetic materials.

The continuum mechanics of solids and fluids serves as the prototypical example of the strategy of turning a blind eye to some subset of the full set of microscopic degrees of freedom. From a continuum perspective, the deformation of the material is captured kinematically through the existence of displacement or velocity fields, while the forces exerted on one part of the continuum by the rest are described via a stress tensor field. For many problems of interest to the mechanical behavior of materials, it suffices to build a description purely in terms of deformation fields and their attendant forces. A review of the key elements of such theories is the subject of this chapter. However, we should also note that the purview of continuum models is wider than that described here, and includes generalizations to liquid crystals, magnetic materials, superconductors and a variety of other contexts.

As noted above, one of the central advantages that comes with the use of continuum models is that they reduce the complexity of description of the material



Fig. 2.1. High-resolution electron micrograph showing a periodic array of Lomer misfit dislocations for an annealed CdTe/GaAs interface. Inset magnifies the two half-planes associated with the perfect pure edge Lomer dislocation (courtesy of Alan Schwartzman).

system. To see this clearly, consider the treatment of a dislocated region of a crystal with dimensions on the order of a micron on a side. This situation is shown from the perspective of high-resolution transmission electron microscopy in fig. 2.1. The figure illustrates the presence of a series of lattice defects at an interface in a semiconductor alloy. What we are to note is that in the immediate neighborhoods of the dislocations there is a significant departure of the atomic positions from their preferred crystalline positions. For the moment, we consider only the geometric description of these deformations without reference to additional complexities that would arise if we chose to consider the chemical disposition of the system as well. Explicit reckoning of the atomistic degrees of freedom in the area of interest would involve on the order of at least 10<sup>10</sup> atoms. In principle, this implies, in turn, the necessity to solve  $10^{10}$  coupled differential equations of motion. By way of contrast, when viewed from the perspective of continuum mechanics, the deformation problem necessitates the use of only three distinct displacement fields which satisfy three coupled partial differential equations. In most instances (at least in the far field regions), the post-processing that would be involved in discovering the relevant linear combinations of the atomistic degrees of freedom is implicit in the existence of the continuum fields themselves. That is, the field variables reflect the collective behavior of the atomic degrees of freedom that is germane to the observed material response. We begin with an analysis of how such kinematic reduction is accomplished.

Broadly speaking, our description of continuum mechanics will be divided along a few traditional lines. First, we will consider the kinematic description of deformation without searching for the attributes of the forces that lead to a particular state of deformation. Here it will be shown that the displacement fields themselves do not cast a fine enough net to sufficiently distinguish between rigid body motions, which are often of little interest, and the more important *relative* motions that result in internal stresses. These observations call for the introduction of other kinematic measures of deformation such as the various strain tensors. Once we have settled these kinematic preliminaries, we turn to the analysis of the forces in continua that lead to such deformation, and culminate in the Cauchy stress principle.

With the tools described above in hand, we can then turn to an analysis of the various balance laws (i.e. linear and angular momentum, energy) that preside over our continuum and to exploring the implications of these balance laws for the solution of the boundary value problems that arise in the modeling of materials. To fully specify a boundary value problem, a constitutive model which relates forces and deformations must be supplied. One of the significant meeting points of the types of continuum and microscopic models we are attempting to link in this book is that of constitutive models. The equations of continuum dynamics are sufficiently generic to describe continuum problems ranging from the stretching of rubber to the breaking of waves. As a result, there is a freedom of description in the generic continuum setting that must be filled in by models of material response. Here, the point is to determine models of material behavior that are sufficiently rich to reflect the roles of the various experimental and microstructural parameters that govern material behavior, without at the same time becoming mired in computational intractability. Historically, the paradigmatic example of such a model is provided by the linear theory of elasticity which is a natural outgrowth of Hooke's law, and often suffices to describe solids that have suffered small deformations. Indeed, later in this chapter we will illustrate the ways in which linear elastic analyses can even be applied to the treatment of highly nonlinear phenomena such as plasticity and fracture. There, we will see that linear elastic analyses provide a wealth of insights into the behavior of the key defects governing plasticity and fracture, namely, dislocations and cracks.

#### 2.2 Kinematics: The Geometry of Deformation

Continuum theories have a number of generic features, one of which is the use of some set of field variables for characterizing the disposition of the system of interest. In the context of the thermodynamics of gases, pressure, volume and temperature may suffice while for electromagnetic media, the electric and magnetic fields play a similar role. For the purposes of constructing continuum models of the mechanical response of deformable bodies, a crucial subset of the required field variables are those describing the geometry of deformation. The business of kinematics is to provide the tools for characterizing the geometric state of a deformed body.

## 2.2.1 Deformation Mappings and Strain

To formalize our treatment of deformation in materials, we introduce the notion of a deformation mapping which is based upon the selection of some reference state which serves as the basis for analysis of the deformed state. The definition of local regions within the continuum is predicated upon the slightly ambiguous notion of a 'material particle' which is imagined to be a sufficiently large region on the scale of the subscale geometries being integrated out (e.g. the crystal lattice or the various grains making up a polycrystalline microstructure), but still small on the scale of the spatial variations in the relevant field variables. As hinted at above, we find it convenient to label material particles in the reference configuration by their position vectors X. The idea of seeking to label each material particle is the continuum analog of the labeling of particles already familiar from discrete particle Newtonian mechanics. In discrete particle mechanics, each and every particle is labeled by an integer, while by contrast, since a continuum by definition has an infinite set of degrees of freedom, we label the particles here by their positions in some reference state. The position of such a material particle at time t after deformation is given by a vector valued function,  $\mathbf{x} = \mathbf{x}(\mathbf{X}, t)$ , known as the deformation mapping. The relation between the reference and deformed configurations is shown in fig. 2.2. It is convenient to define displacement fields  $\mathbf{u}(\mathbf{X}, t)$  such that  $\mathbf{x}(t) = \mathbf{X} + \mathbf{u}(\mathbf{X}, t)$ . We will see below that often, it is more transparent to center attention on the displacement fields themselves instead of the deformation mapping, though the descriptions are equivalent.

For the purposes of examining the geometry of deformation locally, one strategy that is particularly enlightening is to focus our attention on some small neighborhood of the material particle of interest and to examine the changes in the infinitesimal vectors separating it from nearby material points. This strategy may be quantified by centering our attention on the linear part of the deformation mapping as follows. Prior to deformation, the infinitesimal vector that separates neighboring material points is given by  $d\mathbf{X}$ . After deformation, the point at  $\mathbf{X}$  is carried into the point  $\mathbf{x}(\mathbf{X})$ , while the point initially at  $\mathbf{X} + d\mathbf{X}$  is carried into the point  $\mathbf{x}(\mathbf{X} + d\mathbf{X})$ , which may be linearized to yield the mapping



Fig. 2.2. Schematic indicating the relation between reference and deformed states of a material. The vector **X** characterizes the position of a material point before deformation while **x** characterizes the position of the material particle after deformation. The displacement field  $\mathbf{u}(\mathbf{X}, t)$  characterizes the displacement of the material particle at **X**.

Here we have introduced a tensor  $\mathbf{F}$  known as the deformation gradient tensor whose components reflect the various gradients in the deformation mapping and are given by

$$F_{ij} = \frac{\partial x_i}{\partial X_j}.$$
(2.2)

Use of the fact that the deformation mapping may be written as  $\mathbf{x}(t) = \mathbf{X} + \mathbf{u}(\mathbf{X}, t)$ reveals that the deformation gradient may be written alternatively as

$$\mathbf{F} = \mathbf{I} + \nabla \mathbf{u},\tag{2.3}$$

or in indicial notation as  $F_{ij} = \delta_{ij} + u_{i,j}$ .

Once we have determined  $\mathbf{F}$ , we may query a particular state of deformation as to the disposition of the vector  $d\mathbf{X}$  as a result of the deformation. For example, the simplest question one might ask about the vector between two neighboring material particles is how its length changes under deformation. To compute the length change, we compute the difference

$$dl^2 - dL^2 = d\mathbf{x} \cdot d\mathbf{x} - d\mathbf{X} \cdot d\mathbf{X}, \qquad (2.4)$$

where dl is the length of the material element after deformation and dL is the length of the same material element prior to deformation. This expression may be rewritten in terms of the deformation gradient tensor by making the observation that  $d\mathbf{x} = \mathbf{F} d\mathbf{X}$  and hence,

$$dl^{2} - dL^{2} = d\mathbf{X} \cdot (\mathbf{F}^{T}\mathbf{F} - \mathbf{I}) \cdot d\mathbf{X}, \qquad (2.5)$$

where  $\mathbf{F}^T$  denotes the transpose of the deformation gradient tensor. One of our aims is the determination of a measure of deformation that fully accounts for the relative motions associated with internal stresses while at the same time remaining blind to any superposed rigid body motions. This inspires the definition of an auxiliary deformation measure known as the Lagrangian strain tensor and given by

$$\mathbf{E} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I}).$$
(2.6)

The strain tensor provides a more suitable geometric measure of relative displacements, and in the present context illustrates that the length change between neighboring material points is given by

$$dl^2 - dL^2 = 2d\mathbf{X} \cdot \mathbf{E} \cdot d\mathbf{X}.$$
 (2.7)

In addition to the use of the strain to deduce the length change as a result of deformation, it is possible to determine the ways in which angles change as well. The interested reader is invited either to deduce such results for him or herself or to consult any of the pertinent references at the end of the chapter.

For both mathematical and physical reasons, there are many instances in which the spatial variations in the field variables are sufficiently gentle to allow for an approximate treatment of the geometry of deformation in terms of linear strain measures as opposed to the description including geometric nonlinearities introduced above. In these cases, it suffices to build a kinematic description around a linearized version of the deformation measures discussed above. Note that in component form, the Lagrangian strain may be written as

$$E_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i} + u_{k,i}u_{k,j}).$$
(2.8)

Here we have used the fact that  $F_{ij} = \delta_{ij} + u_{i,j}$ . In addition, we have invoked the summation convention in which all repeated indices (in this case the index *k*) are summed over. For the case in which all the displacement gradient components satisfy  $u_{i,j} \ll 1$ , the final term in the expression above may be neglected, resulting in the identification of the 'small strain' (or infinitesimal strain) tensor,

$$\epsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}).$$
 (2.9)

As we will see in subsequent chapters, for many purposes (e.g. the linear theory of elasticity) the small-strain tensor suffices to characterize the deformation of the medium.

The ideas introduced in this section provide a skeletal description of some of the ways in which the geometric deformations in solids are considered. To provide a more concrete realization of these ideas, we now introduce several case studies



Fig. 2.3. Rigid body deformation involving a rotation through an angle  $\theta$  and a translation by the vector **c**.

in the geometry of deformation that will be of particular interest in subsequent chapters.

## 2.2.2 Geometry of Rigid Deformation

Many of the most important deformation mappings in solids can be reduced to one of a few different key types of deformation. One example of a deformation mapping that is enlightening is that of a rigid body motion in which a body is rotated through an angle  $\theta$  about a particular axis and suffers a translation characterized by the vector **c**. An example of this type of deformation is shown in fig. 2.3. The deformation mapping in the case of a rigid body deformation may be written as

$$\mathbf{x}(t) = \mathbf{Q}(t)\mathbf{X} + \mathbf{c}(t), \qquad (2.10)$$

where **Q** is an orthogonal tensor (i.e.  $\mathbf{Q}\mathbf{Q}^T = \mathbf{I}$ ) which results in a rigid body rotation, while **c** is a constant vector and corresponds to a rigid body translation. For the particular case shown in fig. 2.3, the matrix **Q** is given by

$$\mathbf{Q} = \begin{pmatrix} \cos\theta & -\sin\theta & 0\\ \sin\theta & \cos\theta & 0\\ 0 & 0 & 1 \end{pmatrix}, \tag{2.11}$$

a familiar rotation matrix for the case in which the *z*-axis is the axis of rotation.

Application of the definition of the deformation gradient introduced earlier to the case of rigid body deformation yields  $\mathbf{F} = \mathbf{Q}$ . Recalling that  $\mathbf{Q}$  is orthogonal

and hence that  $\mathbf{Q}^T \mathbf{Q} = \mathbf{I}$  reveals that the Lagrangian strain vanishes for such rigid body motions. On the other hand, the infinitesimal strain tensor is nonzero, an observation that is taken up in detail in the problems at the end of the chapter. This example is of interest in part since it shows that despite the fact that the displacement fields are unable to distinguish between uninteresting rigid body motions and deformations involving *relative* motions of material particles, the Lagrangian strain weeds out rigid body deformations. Our reason for making this distinction is the claim that it is the relative motions of material particles that induce internal forces that correspond to our intuitive sense of the stiffness of a material. Despite the existence of nonzero displacements (potentially large), the deformation mapping given above implies no relative motions of material particles and is thus irrelevant to the production of internal stresses.

## 2.2.3 Geometry of Slip and Twinning

In addition to the importance that attaches to rigid body motions, shearing deformations occupy a central position in the mechanics of solids. In particular, permanent deformation by either dislocation motion or twinning can be thought of as a shearing motion that can be captured kinematically in terms of a shear in a direction  $\mathbf{s}$  on a plane with normal  $\mathbf{n}$ .

For simplicity, we begin by considering the case in which the shear is in the  $x_1$ -direction on a plane with normal  $\mathbf{n} = (0, 0, 1)$ , an example of which is shown in fig. 2.4. In this case, the deformation mapping is

$$x_1 = X_1 + \gamma X_3, \tag{2.12}$$

$$x_2 = X_2,$$
 (2.13)

$$x_3 = X_3.$$
 (2.14)

Using the definition of the deformation gradient (i.e.  $F_{ij} = \partial x_i / \partial X_j$ ) we see that in this case we have

$$\mathbf{F} = \begin{pmatrix} 1 & 0 & \gamma \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{2.15}$$

which can be written as

$$\mathbf{F} = \mathbf{I} + \gamma \, \mathbf{e}_1 \otimes \mathbf{e}_3. \tag{2.16}$$

Here we make the key observation that it is only the perpendicular distance from the shearing plane that determines the magnitude of the shearing displacement. In the more general setting characterized by shear direction  $\mathbf{s}$  and shearing plane with



Fig. 2.4. Shear deformation.

normal **n**, we see that the deformation gradient may be written as

$$\mathbf{F} = \mathbf{I} + \gamma \mathbf{s} \otimes \mathbf{n}, \tag{2.17}$$

where  $\gamma$  represents the magnitude of the shear. We note that the outer product used in the equation above is defined through its action on a vector **v** through the expression  $(\mathbf{s} \otimes \mathbf{n})\mathbf{v} = \mathbf{s}(\mathbf{n} \cdot \mathbf{v})$ . From a crystallographic perspective, the type of shearing deformations introduced above are most easily contemplated in the context of twinning in which the material on one side of a twinning plane is subject to a uniform shear of the type considered above. The reader is encouraged to work out the details of such twinning deformations in fcc crystals in the problems section at the end of the chapter.

## 2.2.4 Geometry of Structural Transformations

Yet another example of the geometry of deformation of interest to the present enterprise is that of structural transformation. As was evidenced in chap. 1 in our discussion of phase diagrams, material systems admit of a host of different structural competitors as various control parameters such as the temperature, the pressure and the composition are varied. Many of these transformations can be viewed from a kinematic perspective with the different structural states connected by a deformation pathway in the space of deformation gradients. In some instances, it is appropriate to consider the undeformed and transformed crystals as being linked by an affine transformation. A crystal is built up through the repetition



Fig. 2.5. Representation of the tetragonal to monoclinic transformation in  $ZrO_2$  as an affine transformation (adapted from Budiansky and Truskinovsky (1993)).

of basic units with a given lattice point given as an integral linear combination of the form  $\mathbf{R}_{m_1m_2m_3} = m_i\mathbf{a}_i$ , where the set  $\{\mathbf{a}_i\}$  are the so-called Bravais lattice vectors which serve as the basic template for building the entire crystal lattice. The deformation of such lattices is built around the idea that the Bravais lattice vectors before,  $\{\mathbf{a}'_i\}$ , and after,  $\{\mathbf{a}_i\}$ , transformation are linked via  $\mathbf{a}'_i = \mathbf{F}\mathbf{a}_i$ .

There are a number of different examples within which it is possible to describe the kinematics of structural transformation. Perhaps the simplest such example is that of the transformation between a cubic parent phase and a transformed phase of lower symmetry such as a tetragonal structure. We note that we will return to precisely such structural transformations in the context of martensitic microstructures in chap. 10. If we make the simplifying assumption that the transformed axes correspond with those of the parent phase, then the deformation mapping is of the form

$$x_1 = (1 + \alpha) X_1, \tag{2.18}$$

$$x_2 = (1 + \alpha) X_2, \tag{2.19}$$

$$x_3 = (1+\beta)X_3. \tag{2.20}$$

This corresponds in turn to a deformation gradient tensor of the form

$$\mathbf{F} = \begin{pmatrix} 1+\alpha & 0 & 0\\ 0 & 1+\alpha & 0\\ 0 & 0 & 1+\beta \end{pmatrix}.$$
 (2.21)

Another concrete example of a structural transformation is that of  $ZrO_2$  in which the cubic, tetragonal and monoclinic phases are obtained with decreasing temperature. The immediate continuum treatment of this problem is to represent this sequence of structures as being linked by a series of affine deformations. A schematic of the tetragonal to monoclinic transformation is shown in fig. 2.5. On the other hand, in the case of transformations such as that of  $ZrO_2$  between the cubic and tetragonal structures, there are additional internal rearrangements



Fig. 2.6. Illustration of the internal rearrangements that attend the structural transformation in  $\text{ZrO}_2$  (adapted from Finnis *et al.* (1998)). Although the overall shape of the unit cell can be described in terms of an affine deformation characterized by a constant deformation gradient **F**, the individual internal atoms do not transform accordingly.

that cannot be captured by the type of description advocated above, as shown in fig. 2.6. In this case, the key idea is that in the process of the cubic to tetragonal transformation, not only is there an overall change in the Bravais lattice vectors of the type described above, but in addition, there are internal shifts of the oxygen atoms which are above and beyond the simple affine deformation considered already. A full treatment of the kinematics of structural transformation demands a more complete set of degrees of freedom than that envisioned above.

# 2.3 Forces and Balance Laws

## 2.3.1 Forces Within Continua: Stress Tensors

As yet, we have given little attention to the forces that lead to the deformations we have worked to characterize geometrically. Remarkably, forces within continua can be treated in a generic way through the introduction of a single second-rank tensor field. The surprising feature of the continuum stress idea is that despite the severely complicated atomic configurations that are responsible for a given state of stress, the interatomic forces conspire to produce a net response that can be summarized in terms of the six independent components of a tensor quantity known as the Cauchy stress tensor.

We now examine the question of how in continuum mechanics the forces due to material external to the region  $\Omega$  are communicated to it. Note that we will adopt the notation  $\partial \Omega$  to characterize the boundary of the region  $\Omega$ . In simplest terms, forces are transmitted to a continuum either by the presence of 'body forces' or via 'surface tractions'. Body forces are those such as that due to gravity which



Fig. 2.7. Tetrahedral volume element used to illustrate the Cauchy stress principle.

communicate with the interior of the body via some field, and can be written as  $\int_{\Omega} \mathbf{f}(\mathbf{r}) dV$ , where  $\mathbf{f}$  is the force per unit volume at the point of interest. More typically, forces are communicated to bodies by grabbing them on the surface. Such forces are known as surface tractions and yield a net force  $\int_{\partial\Omega} \mathbf{t} dA$ , where  $\mathbf{t}$  is a vector known as the traction vector and has units of force per unit area. In both the cases of body forces and surface tractions, we note that the total force acting on the region of interest (call it  $\Omega$ ) is obtained by summing up the contributions due to body forces and surface tractions and may be written as

Net force on 
$$\Omega = \int_{\partial\Omega} \mathbf{t} dA + \int_{\Omega} \mathbf{f} dV.$$
 (2.22)

The Cauchy stress principle arises through consideration of the equilibrium of body forces and surface tractions in the special case of the infinitesimal tetrahedral volume shown in fig. 2.7. Three faces of the tetrahedron are perpendicular to the Cartesian axes while the fourth face is characterized by a normal **n**. The idea is to insist on the equilibrium of this elementary volume, which results in the observation that the traction vector on an arbitrary plane with normal **n** (such as is shown in the figure) can be determined once the traction vectors on the Cartesian planes are known. In particular, it is found that  $\mathbf{t}^{(n)} = \boldsymbol{\sigma} \mathbf{n}$ , where  $\boldsymbol{\sigma}$  is known as the stress tensor, and carries the information about the traction vectors associated with the Cartesian planes. The simple outcome of this argument is the claim that once one has determined the nature of the tractions on three complementary planes, the tractions on all other planes follow routinely via  $\mathbf{t}^{(n)} = \boldsymbol{\sigma} \mathbf{n}$ . The details of this argument may be worked out by the reader in the problems section at the end of this chapter.

Now that we have the notion of the stress tensor in hand, we seek one additional insight into the nature of forces within solids that will be of particular interest to our discussion of plastic flow in solids. As was mentioned in section 2.2.3, plastic deformation is the result of shearing deformations on special planes. Certain models of such deformation posit the existence of a critical stress on these planes such that once this stress is attained, shearing deformations will commence. To compute the resolved shear stress on a plane with normal  $\mathbf{n}$  and in a direction  $\mathbf{s}$  we begin by noting that the traction vector on this plane is given by

$$\mathbf{t}^{(\mathbf{n})} = \boldsymbol{\sigma} \mathbf{n}.\tag{2.23}$$

To compute the component of this traction vector in the direction of interest (i.e. the resolved shear stress), it is necessary to project the force along the direction of interest via

$$\sigma_{rss} = \mathbf{s} \cdot \boldsymbol{\sigma} \mathbf{n}. \tag{2.24}$$

As will become evident shortly, calculation of the resolved shear stress will serve as a cornerstone of our analysis of plasticity in single crystals.

# 2.3.2 Equations of Continuum Dynamics

Now that we are in possession of a reckoning of the forces that act within a continuum, it is of immediate interest to seek the continuum analog of the second law of motion which presides over the mechanics of discrete particles. It is not obvious on first glance whether the laws of discrete particle mechanics must be somehow supplemented to account for the smearing out of degrees of freedom which takes place in defining a continuum. However, it has been found that by strictly generalizing the notions of discrete particle mechanics to the continuum setting, this forms a sufficient conceptual backdrop for most purposes. To make this generalization it is first necessary to define the linear momentum of the volume element of interest. We restrict our consideration to a subregion of the body which is labeled  $\Omega$ . The linear momentum **P** associated with this region is defined as

$$\mathbf{P} = \int_{\Omega} \rho \mathbf{v} dV, \qquad (2.25)$$

where  $\rho$  is the mass density field and **v** is the velocity field. The principle of balance of linear momentum is the statement that the time rate of change of the

linear momentum is equal to the net force acting on the region  $\Omega$ . This is nothing more than the continuous representation of  $\mathbf{F} = m\mathbf{a}$ . In mathematical terms the continuous representation of this idea is

$$\frac{D}{Dt} \int_{\Omega} \rho \mathbf{v} dV = \int_{\partial \Omega} \mathbf{t} dA + \int_{\Omega} \mathbf{f} dV.$$
(2.26)

It is important to emphasize that  $\Omega$  itself is time-dependent since the material volume element of interest is undergoing deformation. Note that in our statement of the balance of linear momentum we have introduced notation for our description of the time derivative which differs from the conventional time derivative, indicating that we are evaluating the material time derivative. The material time derivative evaluates the time rate of change of a quantity for a given material particle. Explicitly, we write

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla, \qquad (2.27)$$

where the first term accounts for the explicit time dependence and the second arises in response to the convective terms.

This notation is not an accident and represents a novel feature that arises in the continuum setting as a result of the fact that there are two possible origins for the time dependence of field variables. First, there is the conventional explicit time dependence which merely reflects the fact that the field variable may change with time. The second source of time dependence is a convective term and is tied to the fact that as a result of the motion of the continuum, the material particle can be dragged into a region of space where the field is different. As a concrete realization of this idea, we might imagine a tiny ship sailing in a stream, armed with a thermometer which measures the temperature of the water at the material point being convected with the boat itself. Clearly, one way in which the temperature Tcan vary with time, even if the fluid is at rest, is in the presence of heating which will change the temperature of the fluid and result in a nonzero DT/Dt because of the  $\partial_t T$  term. By way of contrast, we can similarly imagine a time-independent temperature distribution but with the added feature that the temperature of the water is varying along the downstream direction. In this instance, the temperature associated with a given material particle can change by virtue of the fact that the material particle enters a series of spatial regions with different temperatures. In particular, if we imagine a steady flow in the x-direction with velocity  $v_x$ , then DT/Dt will be nonzero because of the term  $v_x \partial_x T$ .

Though the integral form of linear momentum balance written above as eqn (2.26) serves as the starting point of many theoretical developments, it is also convenient to cast the equation in local form as a set of partial differential equations. The idea is to exploit the Reynolds transport theorem in conjunction

with the divergence theorem. For further details on various transport theorems, see chap. 5 of Malvern (1969). The Reynolds transport theorem allows us to rewrite the left hand side of the equation for linear momentum balance as

$$\frac{D}{Dt} \int_{\Omega} \rho \mathbf{v} dV = \int_{\Omega} \rho \frac{D \mathbf{v}}{Dt} dV.$$
(2.28)

The logic behind this development is related to the equation of continuity which asserts the conservation of mass and may be written as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \tag{2.29}$$

This result insures that when we pass the material time derivative operator through the integral as in eqn (2.28), the result is of the form given above. Working in indicial form, we note that using the divergence theorem we may rewrite the term involving surface tractions on the right hand side of eqn (2.26) as

$$\int_{\partial\Omega} \sigma_{ij} n_j dA = \int_{\Omega} \sigma_{ij,j} dV.$$
(2.30)

Thus, eqn (2.26) may be rewritten as

$$\int_{\Omega} \left( \sigma_{ij,j} + f_i - \rho \frac{Dv_i}{Dt} \right) dV = 0.$$
(2.31)

If we now recognize that the choice of our subregion  $\Omega$  was arbitrary we are left with

$$\sigma_{ij,j} + f_i = \rho \frac{Dv_i}{Dt}.$$
(2.32)

This equation is the main governing equation of continuum mechanics and presides over problems ranging from the patterns formed by clouds to the evolution of dislocation structures within metals. Note that as yet no constitutive assumptions have been advanced rendering this equation of general validity. We will find later that for many problems of interest in the modeling of materials it will suffice to consider the static equilibrium version of this equation in which it is assumed that the body remains at rest. In that case, eqn (2.32) reduces to

$$\sigma_{ij,j} + f_i = 0. (2.33)$$

Just as it is possible to generalize the notion of linear momentum to our continuum volume, we can also consider the angular momentum associated with such a material element which is defined by

$$\mathbf{H} = \int_{\Omega} \rho \mathbf{r} \times \mathbf{v} dV. \tag{2.34}$$

Following the prescription adopted above, we assert that angular momentum balance implies

$$\frac{D}{Dt} \int_{\Omega} \rho \mathbf{r} \times \mathbf{v} dV = \int_{\partial \Omega} \mathbf{r} \times \mathbf{t} dA + \int_{\Omega} \mathbf{r} \times \mathbf{f} dV.$$
(2.35)

In indicial form, this may be simplified once we make the identification that  $t_k = \sigma_{km}n_m$  and that the Reynolds transport theorem is still in effect. Bringing all terms to one side and carrying out the appropriate derivatives yields

$$\int_{\Omega} \epsilon_{ijk} \left( \rho v_j v_k + \rho x_j \frac{D v_k}{D t} - x_j \sigma_{km,m} - x_{j,m} \sigma_{km} - x_j f_k \right) dV = 0.$$
(2.36)

We have adopted the convention that the position vector be written in component form as  $\mathbf{r} = x_i \mathbf{e}_i$ . Now we recognize that upon factoring out  $x_j$ , three of these terms are a restatement of linear momentum balance, and are thus zero. In addition, the term involving  $v_j v_k$  also clearly yields zero since it is itself symmetric and is contracted with the antisymmetric Levi-Cevita symbol,  $\epsilon_{ijk}$ . The net result is that we are left with  $\epsilon_{ijk}\sigma_{kj} = 0$  which immediately implies that the stress tensor itself is symmetric. Hence, in the present setting we have seen that the balance of angular momentum implies the symmetry of the Cauchy stress tensor. We also note that in addition to the balance laws for mass, linear momentum and angular momentum presented above, the conservation of energy can be stated in continuum form and the interested reader is referred to texts such as that of Gurtin (1981) referred to at the end of the chapter.

#### 2.3.3 Configurational Forces and the Dynamics of Defects

Earlier in this section we introduced the stress tensor as the tool for describing forces within materials that have been represented as continua. The aim of the present section is to describe a second class of forces within solids that are of particular interest to the mechanics of materials. Materials science is replete with examples of problems in which the notion of a 'driving force' is invoked to explain the temporal evolution of a given configuration. For example, in the context of nucleation, one speaks of a driving force underlying the tendency of a given nucleus to continue its growth. This driving force derives from the reduction in the bulk free energy due to the particle being nucleated. On the other hand, there is an opposing driving force tending to reduce the particle size since the interface will move in a way that minimizes the overall interfacial area, thereby lowering the interfacial contribution to the free energy. Examples of this type can all be brought within the same theoretical fold by recourse to the theory of configurational forces.

The notion of a configurational force is entirely in keeping with our aim of developing effective theories for characterizing the behavior of materials. In
particular, the use of configurational forces allows us to remove our attention from the point by point reckoning of forces demanded both in atomic-level descriptions and continuum notions of stress and, instead, to focus on the effective degrees of freedom introduced to describe defects. As a result, the dynamics of the continuum which demands that we account for the relevant field variables everywhere within the body is replaced with an explicit dynamics of defects in which the kinematics of the defected body is tied only to a set of degrees of freedom that characterize the configuration of the defects themselves. For example, we will see later that despite the fact that dislocations carry with them long-range stress fields, an effective theory of dislocation dynamics can be built in which rather than keeping track of stresses and strains at all points in the continuum, the kinematic description is reduced to a set of nodal coordinates describing the positions of the dislocations. Similarly, in treating the dynamics of interfacial motion, our entire kinematic description can be built around the consideration of coordinates describing the position of the interface.

The central observation associated with the definition of configurational forces is that the total energy of the body of interest and associated loading devices depends explicitly on the positions of the various defects within that body. A small excursion of a given defect from position  $x_i$  to  $x_i + \delta \xi_i$  will result in an attendant change of the total energy. The configurational force on that defect associated with that motion is defined via

$$\delta E_{tot} = -F_i \delta \xi_i. \tag{2.37}$$

This definition may be elaborated alternatively as

$$F_i = -\frac{\partial E_{tot}}{\partial \xi_i}.$$
(2.38)

As noted above, the notion of a configurational force may be advanced as a basis for considering the dynamics of defects themselves since, once such forces are in hand, the temporal evolution of these defects can be built up in turn by the application of an appropriate kinetic law which postulates a relation of the form  $\mathbf{v} = \mathbf{v}(\text{driving force})$ .

To further elaborate the underlying idea of a configurational force, we appeal to the examples indicated schematically in fig. 2.8. Fig. 2.8(a) shows an interface within a solid and illustrates that by virtue of interfacial motion the area of the interface can be reduced. If we adopt a model of the interfacial energy in which it is assumed that this energy is isotropic (i.e.  $\gamma$  does not depend upon the local interface normal **n**), the driving force is related simply to the local curvature of that interface. Within the theory of dislocations, we will encounter the notion of image dislocations as a way of guaranteeing that the elastic fields for dislocations in finite



Fig. 2.8. Representative examples of the origins of the concept of configurational forces: (a) curved interface, (b) dislocation near a free surface and (c) solid with a crack.

bodies satisfy the free surface boundary conditions. What is noted in fig. 2.8(b) is that because of the free surface, a small motion of the subsurface dislocation will result in an attendant energy change and hence in the existence of an image force. Within the present setting, we will see that such image forces are a manifestation of the more general notion of a configurational force. Yet another example of the energy changes that attend the motion of defects is shown in fig. 2.8(c) in which a crack is shown to have suffered an excursion by the amount  $\delta a$ . In this instance, there is a competition between the energy cost to create new free surface, which leads to an energy penalty for incremental crack extension, and the reduction in the elastic strain energy associated with such motions.

Though we have discussed the idea of a configurational force primarily through appeal to specific examples and the generic definition of eqn (2.37), Eshelby pioneered (for example, Eshebly (1975b)) a way of recasting these ideas in an abstract form that is indifferent to the particulars described above. His argument is made on the basis of the observation that because of the broken translational invariance in the types of systems described above, there is an *explicit* dependence of the total energy on the position of the defect. Continuing with the dislocation example given in fig. 2.8(b), we first note that if this single dislocation were embedded in an infinite medium, the elastic energy would not depend explicitly on the position of the dislocation. In particular, we note that

$$\int_{\Omega_{\infty}} \frac{1}{2} \sigma_{ij}^{dis}(\mathbf{x} - \mathbf{x}_0) \epsilon_{ij}^{dis}(\mathbf{x} - \mathbf{x}_0) dV = \int_{\Omega_{\infty}} \frac{1}{2} \sigma_{ij}^{dis}(\mathbf{x} - \mathbf{x}_0 - \delta \boldsymbol{\xi}) \epsilon_{ij}^{dis}(\mathbf{x} - \mathbf{x}_0 - \delta \boldsymbol{\xi}) dV,$$
(2.39)

which is the assertion that whether the dislocation is positioned at position  $\mathbf{x}_0$  or  $\mathbf{x}_0 + \delta \boldsymbol{\xi}$ , the stored energy is the same. To be explicit about notation,  $\Omega_{\infty}$  refers to the fact that the dislocation is in an infinite body and  $\sigma_{ij}^{dis}(\mathbf{x} - \mathbf{x}_0)$  refers to the  $ij^{th}$  component of stress due to a dislocation located at position  $\mathbf{x}_0$ , while  $\epsilon_{ij}^{dis}(\mathbf{x} - \mathbf{x}_0)$  are the corresponding linear elastic strains. By way of contrast with the single dislocation embedded in an infinite medium described above, in the presence of the free surface, the total elastic energy of the system will depend explicitly on the distance of the dislocation beneath the free surface. As a result of this explicit dependence on configuration, there will be a corresponding configurational force.

In light of the definition of the configurational force given above, we may exploit this explicit dependence of the elastic energy on the position of the defect to rewrite the force as

$$F_l = \int_{\Omega} \left( \frac{\partial W}{\partial x_l} \right)_{explicit} dV.$$
(2.40)

*W* is the elastic strain energy density, and the subscript *explicit* reiterates our strategy of picking off the explicit dependence of the total elastic energy on the defect coordinates. As our expression stands, it is nothing more than a schematic representation of the physical origins of the configurational force. To give the equation substance, we must compute  $(\partial W/\partial x_l)_{explicit}$  itself. To do so, we note that the change in the strain energy with position has implicit contributions in addition to those that arise from the symmetry breaking. In particular, the derivative of the strain energy with respect to the position of the defect involves three terms (at least for a material in which the strain energy density depends only upon the displacements and their first derivatives)

$$\frac{\partial W}{\partial x_l} = \frac{\partial W}{\partial u_i} u_{i,l} + \frac{\partial W}{\partial u_{i,j}} u_{i,jl} + \left(\frac{\partial W}{\partial x_l}\right)_{explicit}.$$
(2.41)

Note that the first two terms on the right hand side tell us that there is a change in the strain energy density that is incurred because the defect has moved and it has dragged its elastic fields with it. However, these terms do not reflect the presence of broken translational invariance. By exploiting equality of mixed partials, and by rearranging terms via a simple application of the product rule for differentiation, this expression may be rewritten as

$$\frac{\partial W}{\partial x_l} = \left[\frac{\partial W}{\partial u_i} - \frac{\partial}{\partial x_j} \left(\frac{\partial W}{\partial u_{i,j}}\right)\right] u_{i,l} + \frac{\partial}{\partial x_j} \left[\frac{\partial W}{\partial u_{i,j}}u_{i,l}\right] + \left(\frac{\partial W}{\partial x_l}\right)_{explicit}.$$
 (2.42)

We now note that the term multiplying  $u_{i,l}$  is actually the Euler–Lagrange equation associated with the variational statement of the field equations for the continuum, and thereby vanishes. The net result is that the explicit dependence of the strain

energy density upon position may be computed in terms of the so-called Eshelby tensor as follows:

$$\left(\frac{\partial W}{\partial x_l}\right)_{explicit} = \frac{\partial P_{lj}}{\partial x_j},\tag{2.43}$$

where the Eshelby tensor  $(P_{lj})$  is defined as

$$P_{lj} = W\delta_{lj} - \frac{\partial W}{\partial u_{i,j}} u_{i,l}.$$
(2.44)

The configurational force may now be rewritten as

$$F_i = \int_{\partial\Omega} P_{ij} n_j dA, \qquad (2.45)$$

where we have used the divergence theorem in conjunction with eqn (2.40). This result tells us that by integrating the Eshelby tensor over any surface surrounding the defect of interest, we can find the driving force on that defect. This result can be used in a variety of settings ranging from the derivation of the famed *J*-integral of fracture mechanics to the Peach–Koehler force which describes the force on a dislocation due to a stress.

The theory of configurational forces set forth above is incomplete without some attendant ideas that allow for a determination of the dynamics of defects in the presence of these driving forces. One powerful and convenient set of ideas has been built around variational approaches in which the energy change resulting from the excursion of defects is all dissipated by the mechanisms attending defect motion. Two particularly useful references in that regard are Suo (1997) and Cocks *et al.* (1999). In many ways, the development is entirely analogous to that of conventional analytic mechanics in which for those problems featuring dissipation, the Lagrangian is supplemented with a term known as the Rayleigh dissipation potential. In the present setting, we consider a system whose dissipative excitations are pararameterized with the coordinates ( $\{\mathbf{r}_i\}$ ). For example, this may be a discrete set of points that characterize the position of a dislocation line or an interfacial front. A variational function (or functional for systems whose dissipative excitations are characterized by a continuous set of degrees of freedom) is constructed of the form

$$\Pi(\{\dot{\mathbf{r}}_i\}; \{\mathbf{r}_i\}) = \Psi(\{\dot{\mathbf{r}}_i\}; \{\mathbf{r}_i\}) + G(\{\dot{\mathbf{r}}_i\}; \{\mathbf{r}_i\}), \qquad (2.46)$$

where the first term on the right hand side is the dissipative potential and the second term is the rate of change of the Gibbs free energy. The set  $(\{\mathbf{r}_i\})$  is the complete set of parameters used to specify the configuration of whatever defect(s) are being considered, and the set  $\{\dot{\mathbf{r}}_i\}$  is the associated set of velocities which serve as our variational parameters. What this means is that at a fixed configuration (specified

by the parameters ({ $\mathbf{r}_i$ })), we seek those generalized velocities which are optimal with respect to  $\Pi$ . Note that we have replaced the description of the system either in terms of the atomic coordinates ({ $\mathbf{R}_i$ }) or the field variables  $\mathbf{u}(\mathbf{x})$  with a new set of degrees of freedom that make reference only to the 'coordinates' of the defects themselves. A dynamics of the degrees of freedom ({ $\mathbf{r}_i$ }) is induced through an appeal to the variational statement  $\delta \Pi = 0$ . What this statement means is that the dynamics of the ({ $\mathbf{r}_i$ }) is chosen such that the rate of working on the system, as represented by  $\dot{G}$ , is entirely spent in operating the various dissipative mechanisms that are accounted for in  $\Psi$ . Since our aim is to find velocity increments to step forward in time from a given configuration, for a discrete set of dissipative excitations,  $\delta \Pi = 0$  amounts to the condition that  $\partial \Pi / \partial \dot{\mathbf{r}}_i = 0$  for all i.

This idea can be illustrated in schematic form through the example of the motion of a single curved interface in two dimensions under the action of curvatureinduced forces. For convenience, we will represent the interface as a function (rather than via a discrete set of parameters as in the discussion of the variational principle above) of a parameter *s* as  $\mathbf{r}(s)$ . In this case, the rate of change of Gibbs free energy is given by

$$\dot{G} = \int_{\Gamma} \gamma_{gb} \kappa(s) v_n(s) ds, \qquad (2.47)$$

where  $\Gamma$  is the boundary curve,  $\gamma_{gb}$  is the grain boundary energy and specifies the energy cost per unit area of interface (which for the moment we assume is isotropic, i.e. no dependence on the grain boundary normal **n**),  $\kappa(s)$  is the local curvature of the interface at position **r**(*s*) and  $v_n(s)$  is the normal velocity of the interface at the same point. The energy dissipation associated with this process is in turn given by

$$\Psi = \int_{\Gamma} \frac{v_n^2(s)}{2M} ds, \qquad (2.48)$$

where we have introduced the parameter M which is a mobility and relates the local velocity and the local driving force through the relation  $v_n = Mf$ . Indeed, f is precisely the configurational force described above, and this part of the argument amounts to making kinetic assumptions. What we note now is that by evaluating the variation in  $\Pi$  we end up with equations of motion for the configurational degrees of freedom that enter in our expressions for the configurational forces.

To drive the point home, simplify the discussion above to the case in which the interface is a circle, thus described by a single degree of freedom R. For simplicity, we ignore all contributions to the driving force except for the curvature-induced terms. The Gibbs free energy is given by  $G = 2\pi R\gamma$ . In this case, all of the

expressions given above collapse to the form

$$\Pi = 2\pi \dot{R}\gamma + 2\pi R \frac{\dot{R}^2}{2M}.$$
(2.49)

We are interested now in determining the dynamical equation for the temporal evolution of this circular interface. To obtain that, we consider variations in  $\dot{R}$  at a fixed instantaneous configuration, which demands that we consider  $\partial \Pi / \partial \dot{R} = 0$ , resulting in the equation of motion

$$\frac{dR}{dt} = -\frac{M\gamma}{R}.$$
(2.50)

Not surprisingly, this equation of motion implies the curvature-induced shrinkage of the particle.

This section has provided two related tools that we will return to repeatedly throughout the book. The first of those tools was the idea of a configurational force, which tells us that if a defect is characterized by some set of coordinates  $({\bf r}_i)$ , then there is a set of forces conjugate to these coordinates such that the change in energy when the defect suffers an excursion  $(\{\delta \mathbf{r}_i\})$  is given by  $\delta E_{tot} =$  $-\sum_{i} \mathbf{F}_{i} \cdot \delta \mathbf{r}_{i}$ . By virtue of the elastic energy-momentum tensor, we have also argued that there is a generic formalism that allows for the determination of these configurational forces, although we wish to emphasize that all that is really needed in the consideration of a given problem is the definition of configurational forces as the work-conjugate partners of the various coordinates used to characterize the position of the defect. We have also seen that there is a variational formalism for inducing a dynamics on the coordinates used to describe the configuration of a given defect. This variational principle selects those trajectories such that the rate of working on the system is balanced by the rate of dissipation that attends the dissipative excitations of the defects. We note again that the ideas presented here serve as the foundation of the construction of effective theories of defects since they allow us to choose the degrees of freedom in a given problem as the defect coordinates themselves, allowing us to abandon a description in terms of either atomic coordinates or continuum fields. The framework described here will be used to consider the motion of cracks and serves as the basis of the development of the J-integral, the motion of dislocations serving as the basis of the deduction of the Peach-Koehler force, the motion of grain boundaries resulting in expressions for both curvature- and diffusion-induced motion of boundaries and will serve as the basis of our discussions of the dynamical simulation of both dislocation dynamics and microstructural evolution.

## 2.4 Continuum Descriptions of Deformation and Failure

## 2.4.1 Constitutive Modeling

Both the power and limitation of continuum mechanics derive from the same origins. On the one hand, the beauty of the continuum approach is its ability to renounce microscopic details. On the other hand, because of this, it is necessary to introduce material specificity into continuum models through phenomenological constitutive models. Recall that in writing the equation for the balance of linear momentum, we have as yet made no reference to whether or not our equations describe the deformation of a polycrystal with a highly anisotropic grain structure or the moments before a wave ends its journey across the ocean in a tumultuous explosion of whitewater. Whether our interest is in the description of injecting polymers into molds, the evolution of Jupiter's red spot, the development of texture in a crystal, or the formation of vortices in wakes, we must supplement the governing equations of continuum mechanics with some constitutive description.

The role of constitutive equations is to instruct us in the relation between the forces within our continuum and the deformations that attend them. More prosaically, if we examine the governing equations derived from the balance of linear momentum, it is found that we have more unknowns than we do equations to determine them. Spanning this information gap is the role played by constitutive models. From the standpoint of building effective theories of material behavior, the construction of realistic and tractable constitutive models is one of our greatest challenges. In the sections that follow we will use the example of linear elasticity as a paradigm for the description of constitutive response. Having made our initial foray into this theory, we will examine in turn some of the ideas that attend the treatment of permanent deformation where the development of microscopically motivated constitutive models is much less mature.

## 2.4.2 Linear Elastic Response of Materials

The linear theory of elasticity is the logical extension and natural generalization of the insights into material behavior that are embodied in Hooke's law. The basic idea is suggested by the types of experiments that were originally considered by Hooke and are depicted in fig. 2.9. The fundamental idea of experiments of this type is to determine a relation between the geometry of deformation and the forces that produce it. The central result for linearly elastic materials is that the strain and stress are linearly related. For the types of geometries shown in the figure, a single scalar relation suffices. For example, in tension experiments, Hooke's law may be stated as



Fig. 2.9. Apparatus used by Robert Hooke in his investigation of the relation between the displacement of a body and the load which produces it (adapted from Bell (1973)).

$$\frac{F}{A} = E \frac{\Delta l}{l},\tag{2.51}$$

where the left hand side of the equation is the force per unit area, and the ratio on the right hand side is the fractional change in length of the specimen. The constant E is the so-called Young's modulus and for this simple test geometry is the point of entry of material specificity into the problem.

Under more complex states of loading, Hooke's law required elaboration. The generalization of Hooke's law is the assertion that an arbitrary component of the

stress tensor may be written in terms of the infinitesimal strains,  $\epsilon_{ij}$ , as follows:

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl}. \tag{2.52}$$

What this equation tells us is that a particular state of stress is nothing more than a linear combination (albeit perhaps a tedious one) of the entirety of components of the strain tensor. The tensor  $C_{ijkl}$  is known as the elastic modulus tensor or stiffness and for a linear elastic material provides nearly a complete description of the material properties related to deformation under mechanical loads. Eqn (2.52) is our first example of a constitutive equation and, as claimed earlier, provides an explicit statement of material response that allows for the emergence of material specificity in the equations of continuum dynamics as embodied in eqn (2.32). In particular, if we substitute the constitutive statement of eqn (2.52) into eqn (2.32) for the equilibrium case in which there are no accelerations, the resulting equilibrium equations for a linear elastic medium are given by

$$C_{ijkl}u_{k,lj} + f_i = 0. (2.53)$$

As usual, we have invoked the summation convention and in addition have assumed that the material properties are homogeneous. For an isotropic linear elastic solid, the constitutive equation relating the stresses and strains is given by

$$C_{ijkl} = \lambda \delta_{ij} \delta_{kl} + \mu (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}), \qquad (2.54)$$

where  $\lambda$  and  $\mu$  are the Lamé constants. Simple substitution and a few lines of algebra yield the so-called Navier equations that serve as the equilibrium equations for an isotropic linear elastic solid,

$$(\lambda + \mu)\nabla(\nabla \cdot \mathbf{u}) + \mu\nabla^2 \mathbf{u} + \mathbf{f} = 0.$$
(2.55)

Note that these equations are a special case of the equilibrium equations revealed in eqn (2.53) in the constitutive context of an isotropic linear elastic solid.

In addition to the characterization of elastic solids in terms of the stress–strain response given in eqn (2.52), linearly elastic materials may also be characterized in terms of a local strain energy density that reveals the energy per unit volume stored in the elastic fields. To the extent that we are interested in describing the energetics of deformations that are sufficiently 'small', the total energy stored in a body by virtue of its deformation is contained in the parameters that make up the elastic modulus tensor. In particular, the total strain energy tied up in the elastic fields is given by

$$E_{strain} = \frac{1}{2} \int_{\Omega} C_{ijkl} \epsilon_{ij} \epsilon_{kl} dV.$$
 (2.56)

As we will see in coming chapters, the logic that rests behind this model is a