EVOLUTION OF PHASE TRANSITIONS

This work began with the authors’ exploration of the applicability of the finite deformation theory of elasticity when various standard assumptions such as convexity of the energy or ellipticity of the field equations of equilibrium are relinquished. The finite deformation theory of elasticity turns out to be a natural vehicle for the study of phase transitions in solids where thermal effects can be neglected. This is a valuable work for those interested in the development and application of continuum-mechanical models that describe the macroscopic response of materials capable of undergoing stress- or temperature-induced transitions between two solid phases. The focus is on the evolution of phase transitions, which may be either dynamic or quasi-static, controlled by a kinetic relation that in the framework of classical thermomechanics represents information that is supplementary to the usual balance principles and constitutive laws of conventional theory. The book should be of interest to mechanicians, material scientists, geophysicists, and applied mathematicians.

Rohan Abeyaratne is the Quentin Berg Professor of Mechanics and Head of the Department of Mechanical Engineering at MIT. He received his bachelor’s degree from the University of Ceylon and his doctorate from the California Institute of Technology. Among his honors are the E.O.E. Pereira Gold Medal (1975), Den Hartog Distinguished Educator (1995), MacVicar Fellowship (2000), Fellow, American Academy of Mechanics (1996) and Fellow, American Society of Mechanical Engineers (1998). His primary research interest is in nonlinear phenomena in mechanics.

James K. Knowles is the William R. Kenan Professor of Applied Mechanics, Emeritus, at the California Institute of Technology. He received his S.B. and Ph.D. degrees from MIT, and he holds an honorary Sc.D. degree from the National University of Ireland. He is a Fellow of the American Academy of Mechanics (AAM), the American Association for the Advancement of Science and the American Society of Mechanical Engineers (ASME). He is a past president of AAM, and he is a recipient of MIT’s Goodwin Medal for teaching, the Eringen Medal of the Society of Engineering Science and the Koiter Medal of the ASME. His primary research interests are in nonlinear phenomena in continuum mechanics, and in analytical issues in fracture mechanics and the theory of elasticity.
EVOLUTION OF PHASE TRANSITIONS
A Continuum Theory

ROHAN ABEYARATNE
Massachusetts Institute of Technology

JAMES K. KNOWLES
California Institute of Technology
To the C7: Gina, Kenny, Kevin, Kristen, Liam, Linus, & Nina;

and the J4: Jackie, John, Jeff, & Jamey.
Contents

Preface ........................................ page xiii

Part I Introduction ............................ page 3
1 Introduction ................................. 3
   1.1 What this monograph is about ........ 3
   1.2 Some experiments ...................... 7
   1.3 Continuum mechanics ................. 9
   1.4 Quasilinear systems ................. 10
   1.5 Outline of monograph ............... 11

Part II Purely Mechanical Theory .......... page 19
2 Two-Well Potentials, Governing Equations
   and Energetics ........................... 19
   2.1 Introduction ............................ 19
   2.2 Two-phase nonlinearly elastic materials 20
   2.3 Field equations and jump conditions 25
   2.4 Energetics of motion, driving force and dissipation
       inequality ............................ 27

3 Equilibrium Phase Mixtures and Quasistatic
   Processes .................................. 32
   3.1 Introduction ............................ 32
   3.2 Equilibrium states .................... 33
   3.3 Variational theory of equilibrium mixtures
       of phases ............................. 37
   3.4 Quasistatic processes ............... 42
   3.5 Nucleation and kinetics ............. 44
   3.6 Constant elongation rate processes  47
   3.7 Hysteresis ............................. 53
# Contents

4 Impact-Induced Transitions in Two-Phase Elastic Materials ........................... 59
   4.1 Introduction 59
   4.2 The impact problem for trilinear two-phase materials 61
      4.2.1 The constitutive law 61
      4.2.2 The impact problem 64
   4.3 Scale-invariant solutions of the impact problem 66
      4.3.1 Solutions without a phase transition 66
      4.3.2 Solutions with a phase transition: The two-wave case 67
      4.3.3 Solutions with a phase transition: The one-wave case 68
      4.3.4 The totality of solutions 69
   4.4 Nucleation and kinetics 71
   4.5 Comparison with experiment 74
   4.6 Other types of kinetic relations 77
   4.7 Related work 77

Part III Thermomechanical Theory

5 Multiple-Well Free Energy Potentials .............. 85
   5.1 Introduction 85
   5.2 Helmholtz free energy potential 86
   5.3 Potential energy function and the effect of stress 88
   5.4 Example 1: The van der Waals Fluid 90
   5.5 Example 2: Two-phase martensitic material with cubic and tetragonal phases 95

6 The Continuum Theory of Driving Force ............ 105
   6.1 Introduction 105
   6.2 Balance laws, field equations and jump conditions 106
      6.2.1 Balances of momentum and energy in integral form 106
      6.2.2 Localization of the balance laws 106
   6.3 The second law of thermodynamics and the driving force 108
      6.3.1 Entropy production rate 108
      6.3.2 Driving force and the second law 110
      6.3.3 Driving force in the case of mechanical equilibrium 111

7 Thermoelastic Materials ........................... 113
   7.1 Introduction 113
   7.2 The thermoelastic constitutive law 113
      7.2.1 Relations among stress, deformation gradient, temperature and specific entropy 113
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2.2</td>
<td>The heat conduction law</td>
<td>116</td>
</tr>
<tr>
<td>7.2.3</td>
<td>The partial differential equations of nonlinear thermoelasticity</td>
<td>116</td>
</tr>
<tr>
<td>7.2.4</td>
<td>Thermomechanical equilibrium</td>
<td>117</td>
</tr>
<tr>
<td>7.3</td>
<td>Stability of a thermoelastic material</td>
<td>118</td>
</tr>
<tr>
<td>7.4</td>
<td>A one-dimensional special case: uniaxial strain</td>
<td>120</td>
</tr>
</tbody>
</table>

### 8 Kinetics and Nucleation .......................... 124

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>124</td>
</tr>
<tr>
<td>8.2</td>
<td>Nonequilibrium processes, thermodynamic fluxes and forces, kinetic relation</td>
<td>124</td>
</tr>
<tr>
<td>8.3</td>
<td>Phenomenological examples of kinetic relations</td>
<td>127</td>
</tr>
<tr>
<td>8.4</td>
<td>Micromechanically based examples of kinetic relations</td>
<td>128</td>
</tr>
<tr>
<td>8.4.1</td>
<td>Viscosity-strain gradient model</td>
<td>130</td>
</tr>
<tr>
<td>8.4.2</td>
<td>Thermal activation model</td>
<td>131</td>
</tr>
<tr>
<td>8.4.3</td>
<td>Propagation through a row of imperfections</td>
<td>133</td>
</tr>
<tr>
<td>8.4.4</td>
<td>Kinetics from atomistic considerations</td>
<td>134</td>
</tr>
<tr>
<td>8.4.5</td>
<td>Frenkel-Kontorowa model</td>
<td>136</td>
</tr>
<tr>
<td>8.5</td>
<td>Nucleation</td>
<td>139</td>
</tr>
</tbody>
</table>

### Part IV One-Dimensional Thermoelastic Theory and Problems

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Models for Two-Phase Thermoelastic Materials in One Dimension</td>
<td>149</td>
</tr>
<tr>
<td>9.1</td>
<td>Preliminaries</td>
<td>149</td>
</tr>
<tr>
<td>9.2</td>
<td>Materials of Mie-Grüneisen type</td>
<td>151</td>
</tr>
<tr>
<td>9.3</td>
<td>Two-phase Mie-Grüneisen materials</td>
<td>153</td>
</tr>
<tr>
<td>9.3.1</td>
<td>The trilinear material</td>
<td>153</td>
</tr>
<tr>
<td>9.3.2</td>
<td>Stability of phases of the trilinear material</td>
<td>156</td>
</tr>
<tr>
<td>9.3.3</td>
<td>Other two-phase materials of Mie-Grüneisen type</td>
<td>159</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Quasistatic Hysteresis in Two-Phase Thermoelastic Tensile Bars</td>
<td>163</td>
</tr>
<tr>
<td>10.1</td>
<td>Preliminaries</td>
<td>163</td>
</tr>
<tr>
<td>10.2</td>
<td>Thermomechanical equilibrium states</td>
<td>164</td>
</tr>
<tr>
<td>10.3</td>
<td>Quasistatic processes</td>
<td>166</td>
</tr>
<tr>
<td>10.4</td>
<td>Trilinear thermoelastic material</td>
<td>167</td>
</tr>
<tr>
<td>10.5</td>
<td>Stress cycles at constant temperature</td>
<td>169</td>
</tr>
<tr>
<td>10.6</td>
<td>Temperature cycles at constant stress</td>
<td>173</td>
</tr>
</tbody>
</table>
10.7 The shape-memory cycle 175
10.8 The experiments of Shaw and Kyriakides 176
10.9 Slow thermomechanical processes 178

11 Dynamics of Phase Transitions in Uniaxially Strained Thermoelectric Solids .......................... 181
11.1 Introduction 181
11.2 Uniaxial strain in adiabatic thermoelasticity 182
11.2.1 Field equations, jump conditions and driving force 182
11.2.2 The trilinear Mie-Grüneisen thermoelastic material 183
11.3 The impact problem 185
11.3.1 Formulation: Scale-invariant solutions 185
11.3.2 Solutions with no phase transition 186
11.3.3 Solutions with a phase transition 188

Part V Higher Dimensional Problems

12 Statics: Geometric Compatibility .................. 197
12.1 Preliminaries 197
12.2 Examples 200

13 Dynamics: Impact-Induced Transition in a CuAlNi Single Crystal .............................................. 209
13.1 Introduction 209
13.2 Preliminaries 210
13.3 Impact without phase transformation 212
13.4 Impact with phase transformation 214
13.5 Application to austenite-$\beta'$ martensite transformation in CuAlNi 217
13.5.1 Experimental data 217
13.5.2 Phase boundary speed 218
13.5.3 Driving force 218
13.5.4 Kinetic law 219

14 Quasistatics: Kinetics of Martensitic Twinning ........ 221
14.1 Introduction 221
14.2 The material and loading device 222
14.3 Observations 223
14.4 The model 225
14.5 The energy of the system 226
14.5.1 Elastic energy of the specimen 226
14.5.2 Loading device energy 227
14.5.3 Summary 228
CONTENTS

14.6 The effect of the transition layers: Further observations 229
14.7 The effect of the transition layers: Further modeling 230
14.8 Kinetics 231

Author Index ........................................... 235
Subject Index .......................................... 238
Preface

This monograph threads together a series of research studies carried out by the authors over a period of some fifteen years or so. It is concerned with the development and application of continuum-mechanical models that describe the macroscopic response of materials capable of undergoing stress- or temperature-induced transitions between two solid phases.

Roughly speaking, there are two types of physical settings that provide the motivation for this kind of modeling. One is that associated with slow mechanical or thermal loading of alloys such as nickel–titanium or copper–aluminum–nickel that exhibit the shape-memory effect. The second arises from high-speed impact experiments in which metallic or ceramic targets are struck by moving projectiles; the objective of such studies – often of interest in geophysics – is usually to determine the response of the impacted material to very high pressures. Phase transitions are an essential feature of the shape-memory effect, and they frequently occur in high-speed impact experiments on solids. Those aspects of the theory presented here that are purely phenomenological may well have broader relevance, in the sense that they may be applicable to materials that transform between two “states,” for example, the ordered and disordered states of a polymer.

Our development focuses on the evolution of the phase transitions modeled here, which may be either dynamic or quasistatic. Such evolution is controlled by a “kinetic relation,” which, in the framework of classical thermomechanics, represents information supplementary to the usual balance principles and constitutive laws of conventional theory. We elucidate the rather remarkable way in which the classical theory “calls for” this kind of supplementary information when the material is capable of changing phase, though such additional information is not called for – indeed, cannot be imposed – in the case of a single-phase material.

The simplest context in which to illustrate the need for kinetic relations and the role they play is that furnished by the purely mechanical theory of one-dimensional nonlinear elasticity, with thermal effects suppressed. After the Introduction, which comprises Part I of the monograph, we pursue the subject in this context in Part II. Even this simplest version of the theory to be set out here has some utility, as we show in Chapters 3 and 4. Part III presents the full three-dimensional theory, taking
both mechanical and thermal effects into account. We specialize this theory to one space dimension in Part IV, where we are able to make some comparisons with experiments. In Part V, we discuss some three-dimensional problems.

The material presented here is drawn primarily from our own research over the period from the late 1980s forward. We came to this subject as practitioners of solid mechanics interested in exploring the range of applicability of the finite deformation theory of elasticity when various standard assumptions such as convexity of various energies or ellipticity of the field equations of equilibrium were relinquished. When broadened in this way, finite elasticity is a natural vehicle for the study of those aspects of phase transitions in solids that can be discussed with thermal effects neglected. Nonlinear thermoelasticity, similarly unencumbered by conventional restrictions, provides the natural framework for the study of mechanical and thermal effects together.

Our hope is that this book will be of interest to materials scientists, engineers and geophysicists as well as to mechanicians and applied mathematicians. The perfectly prepared reader would be acquainted with continuum mechanics at the level of Chadwick’s *Continuum Mechanics*, Wiley, New York, 1976; with thermodynamics as treated, for example, in J. L. Ericksen’s *Introduction to the Thermodynamics of Solids*, Chapman and Hall, New York, 1991; with material behavior as described by T. H. Courtney in *Mechanical Behavior of Materials*, McGraw-Hill, New York, 1990; with partial differential equations at the level of J. D. Logan’s *An Introduction to Nonlinear Partial Differential Equations*, Wiley-Interscience, New York, 1994; and with the elements of Cartesian tensors as discussed, for example, in *Linear Vector Spaces and Cartesian Tensors*, Oxford, New York, 1998, by J. K. Knowles. However, expecting many potential readers to be less than perfectly prepared, we have tried to make the presentation as self-contained as is practicable, citing appropriate sources for those results that are used but not derived.

Although the book deals almost entirely with our own work, we have nevertheless had the enormous benefit of interactions with many others, and it is a pleasure to acknowledge them all with gratitude. We would be remiss not to mention the particular influence that Tom Ahrens, Kaushik Bhattacharya, Mort Gurtin, Rick James, Stelios Kyriakides, Jim Rice, the late Eli Sternberg, Lev Truskinovsky, and our former doctoral students, especially Phoebus Rosakis and Stewart Silling, have had on our learning of this subject.

Some of the fruitful interactions alluded to above took place in small, informal summer gatherings held at MIT’s Talbot House in South Pomfret, Vermont. We are indebted to MIT for the use of this wonderful place, which — alas — is no longer owned by MIT.

Special thanks go to Debbie Blanchard, who drew the figures in the early part of the book, and then taught us how to draw the rest.

We are grateful to Olaf Weckner for a careful and constructive critical reading of the early chapters.

We acknowledge with thanks the past financial support of the U.S. National Science Foundation, the U.S. Army Research Office, and especially the U.S. Office
of Naval Research, with which we enjoyed a sustained relationship and which supported much of the research on which this monograph is based. We would particularly like to thank Roshdy Barsoum, Alan Kushner, and Yapa Rajapakse for the help and encouragement that they, as program officers at ONR, consistently provided to us.

During recent stimulating visits, both of us have benefited from the hospitality and financial support of the University of Cambridge, its colleges, and its Isaac Newton Institute for the Mathematical Sciences, for which we wish to express our appreciation.

Rohan Abeyaratne and Jim Knowles
Cambridge, Massachusetts, and Pasadena, California
June 2005