Statistical Thermodynamics
An Engineering Approach

Dr. Daily is currently Professor of Mechanical Engineering at the University of Colorado at Boulder. He studied mechanical engineering at the University of Michigan (BS 1968, MS 1969) and at Stanford University (PhD 1975). Prior to starting college he worked on sports and racing cars, owning his own business. Between the MS and PhD degrees he worked as a heat transfer analyst at Aerojet Liquid Rocket Company. After receiving the PhD he was a faculty member at the University of California at Berkeley until 1988, when he moved to the University of Colorado. He has served as the Director of the Center for Combustion Research and as Chair of the Mechanical Engineering Department at the University of Colorado.

His academic career has been devoted to the field of energy, focusing on combustion and environmental studies. He has worked on combustion and heat transfer aspects of propulsion and power generation devices, studying such topics as fluid mechanics of mixing, chemical kinetics, combustion stability, and air pollution. He also works on the development of advanced diagnostic instrumentation (including laser based) for studying reacting flows and environmental monitoring. Most recently he has been working in the areas of biomass thermochemical processing and source characterization, wildfire behavior, the environmental consequences of combustion, and optical biopsy of cancer. He is a founder of Precision Biopsy Inc., a company developing technology for the optical detection of prostate cancer.

Dr. Daily served as a member of the San Francisco Bay Area Air Quality Management District Advisory Council for 10 years. He served on and chaired the State of Colorado Hazardous Waste Commission for over 10 years and was on the State of Colorado Air Quality Control Commission. He is a Fellow of The American Institute of Aeronautics and Astronautics (AIAA) and serves as chair of its Publications Committee.
Statistical Thermodynamics
An Engineering Approach

JOHN W. DAILY
University of Colorado Boulder
Brief Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Figures</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xvi</td>
</tr>
<tr>
<td>Preface</td>
<td>xvii</td>
</tr>
<tr>
<td>Comment on Software</td>
<td>xix</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>xx</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2 Fundamentals of Macroscopic Thermodynamics</td>
<td>9</td>
</tr>
<tr>
<td>3 Microscopic Thermodynamics</td>
<td>36</td>
</tr>
<tr>
<td>4 Quantum Mechanics</td>
<td>57</td>
</tr>
<tr>
<td>5 Ideal Gases</td>
<td>92</td>
</tr>
<tr>
<td>6 Ideal Gas Mixtures</td>
<td>109</td>
</tr>
<tr>
<td>7 The Photon and Electron Gases</td>
<td>122</td>
</tr>
<tr>
<td>8 Dense Gases</td>
<td>132</td>
</tr>
<tr>
<td>9 Liquids</td>
<td>144</td>
</tr>
<tr>
<td>10 Crystalline Solids</td>
<td>156</td>
</tr>
<tr>
<td>11 Thermodynamic Stability and Phase Change</td>
<td>166</td>
</tr>
<tr>
<td>12 Kinetic Theory of Gases</td>
<td>178</td>
</tr>
<tr>
<td>13 Spectroscopy</td>
<td>196</td>
</tr>
<tr>
<td>14 Chemical Kinetics</td>
<td>216</td>
</tr>
<tr>
<td>Appendices</td>
<td>232</td>
</tr>
<tr>
<td>References</td>
<td>257</td>
</tr>
<tr>
<td>Index</td>
<td>261</td>
</tr>
</tbody>
</table>
# Contents

*List of Figures*  
<table>
<thead>
<tr>
<th>List of Figures</th>
<th>page xiii</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Tables</td>
<td>xvi</td>
</tr>
<tr>
<td>Preface</td>
<td>xvii</td>
</tr>
<tr>
<td>Comment on Software</td>
<td>xix</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>xx</td>
</tr>
</tbody>
</table>

## 1 Introduction
1.1 The Role of Thermodynamics | 1
1.2 The Nature of Matter | 2
1.3 Energy, Work, Heat Transfer, and the 1st Law | 2
1.4 Equilibrium | 4
1.5 Thermodynamic Properties | 5
1.6 The Fundamental Problem of Thermodynamics | 6
1.7 Analysis of Non-equilibrium Behavior | 7
1.8 Summary | 7
1.9 Problems | 8

## 2 Fundamentals of Macroscopic Thermodynamics
2.1 The Postulates of Macroscopic (Classical) Thermodynamics | 9
2.2 Simple Forms of the Fundamental Relation | 11
2.2.1 Van der Waals Substance | 12
2.2.2 Ideal Gas | 13
2.3 Equilibrium and the Intensive Properties | 13
2.3.1 Thermal Equilibrium: The Meaning of Temperature | 14
2.3.2 Mechanical Equilibrium: The Meaning of Pressure | 15
2.3.3 Matter Flow and Chemical Equilibrium: The Meaning of Chemical Potential | 16
2.4 Representation and the Equations of State | 17
2.5 The Euler Equation and the Gibbs–Duhem Relation | 18
2.6 Quasi-static Processes and Thermal and Mechanical Energy Reservoirs | 19
2.7 Equilibrium in the Energy Representation | 21
2.8 Alternative Representations – Legendre Transformations | 22
2.8.1 Example 2.1 | 23
Contents

2.9 Transformations of the Energy 24
2.10 Transformations of the Entropy 24
2.11 Reversible Work 25
2.12 Maxwell’s Relations 26
2.13 Building Property Relations 27
2.14 Sources for Thermodynamic Properties 29
2.15 Summary 30
  2.15.1 Postulates and the Fundamental Relation 30
  2.15.2 Equilibrium and Intensive Parameters 31
  2.15.3 Representation and Equations of State 31
  2.15.4 The Euler Equation and the Gibbs–Duhem Relation 32
  2.15.5 Alternative Representations 32
  2.15.6 Maxwell’s Relations 32
  2.15.7 Property Relations 33
2.16 Problems 33

3 Microscopic Thermodynamics 36
  3.1 The Role of Statistics in Thermodynamics 36
  3.2 The Postulates of Microscopic Thermodynamics 40
  3.3 The Partition Function and its Alternative Formulations 41
  3.4 Thermodynamic Properties 43
  3.5 Fluctuations 46
  3.6 Systems with Negligible Inter-particle Forces 48
  3.7 Systems with Non-negligible Inter-particle Forces 52
  3.8 Summary 52
    3.8.1 Statistics in Thermodynamics and Ensembles 52
    3.8.2 The Postulates of Microscopic Thermodynamics 53
    3.8.3 The Partition Function 53
    3.8.4 Relationship of Partition Function to Fundamental Relation 54
    3.8.5 Fluctuations 54
    3.8.6 Systems with Negligible Inter-particle Forces 54
    3.8.7 Systems with Non-negligible Inter-particle Forces 55
  3.9 Problems 55

4 Quantum Mechanics 57
  4.1 A Brief History 57
    4.1.1 Wave–Particle Duality – Electromagnetic Radiation Behaves Like Particles 58
    4.1.2 Particle–Wave Duality – Particles Can Display Wave-Like Behavior 61
    4.1.3 Heisenberg Uncertainty Principle 61
  4.2 The Postulates of Quantum Mechanics 63
  4.3 Solutions of the Wave Equation 64
    4.3.1 The Particle in a Box 66
    4.3.2 Internal Motion 68
## Contents

4.3.3 The Hydrogenic Atom 71  
4.3.4 The Born–Oppenheimer Approximation and the Diatomic Molecule 73  
4.4 Real Atomic Behavior 78  
4.4.1 Pauli Exclusion Principle 78  
4.4.2 Higher-Order Effects 79  
4.4.3 Multiple Electrons 81  
4.5 Real Molecular Behavior 84  
4.6 Molecular Modeling/Computational Chemistry 86  
4.6.1 Example 4.1 87  
4.7 Summary 88  
4.8 Problems 89  

5  
**Ideal Gases**  
5.1 The Partition Function 92  
5.2 The Translational Partition Function 93  
5.3 Monatomic Gases 96  
5.3.1 Example 5.1 96  
5.4 Diatomic Gases 99  
5.4.1 Rotation 99  
5.4.2 Example 5.2 101  
5.4.3 Vibration 102  
5.4.4 Properties 103  
5.5 Polyatomic Gases 105  
5.6 Summary 106  
5.6.1 Monatomic Gas 106  
5.6.2 Simple Diatomic Gas 107  
5.6.3 Polyatomic Molecules 107  
5.7 Problems 108  

6  
**Ideal Gas Mixtures**  
6.1 Non-reacting Mixtures 109  
6.1.1 Changes in Properties on Mixing 110  
6.1.2 Example 6.1 111  
6.2 Reacting Mixtures 112  
6.2.1 General Case 112  
6.2.2 Properties for Equilibrium and 1st Law Calculations 114  
6.2.3 Example 6.2 115  
6.2.4 The Equilibrium Constant 116  
6.2.5 Example 6.3 118  
6.2.6 The Principle of Detailed Balance 119  
6.3 Summary 119  
6.3.1 Non-reacting Mixtures 119  
6.3.2 Reacting Mixtures 120  
6.4 Problems 121
Contents

7 The Photon and Electron Gases
7.1 The Photon Gas
7.1.1 Example 7.1
7.2 The Electron Gas
7.2.1 Example 7.2
7.2.2 Example 7.3
7.3 Summary
7.3.1 Photon Gas
7.3.2 Electron Gas
7.4 Problems

8 Dense Gases
8.1 Evaluating the Configuration Integral
8.2 The Virial Equation of State
8.3 Other Properties
8.4 Potential Energy Functions
8.4.1 Example 8.1
8.4.2 Example 8.2
8.5 Other Equations of State
8.6 Summary
8.6.1 Evaluating the Configuration Integral
8.6.2 Virial Equation of State
8.6.3 Other Properties
8.6.4 Potential Energy Function
8.6.5 Other Equations of State
8.7 Problems

9 Liquids
9.1 The Radial Distribution Function and Thermodynamic Properties
9.1.1 Example 9.1
9.2 Molecular Dynamics Simulations of Liquids
9.3 Determining $g(r)$ from Molecular Dynamics Simulations
9.4 Molecular Dynamics Software
9.4.1 Example 9.2
9.5 Summary
9.6 Problems

10 Crystalline Solids
10.1 Einstein Crystal
10.2 Debye Crystal
10.2.1 Example 10.1
10.3 Summary
10.4 Problems
Contents

13.8.1 The Absorption and Emission of Radiation 213
13.8.2 Spectral Line Broadening 214
13.8.3 Spectral Transitions 214
13.8.4 Types of Spectroscopies 214
13.9 Problems 214

14 Chemical Kinetics 216
14.1 Reaction Rate 216
14.2 Reaction Rate Constant and the Arrhenius Form 217
  14.2.1 Unimolecular Reactions 221
  14.2.2 Example 14.1 222
14.3 More on Reaction Rates 223
  14.3.1 Transition State Theory 224
  14.3.2 Statistical Theories: RRKM 224
14.4 Reaction Mechanisms 226
  14.4.1 Example 14.2 228
14.5 Summary 229
  14.5.1 Reaction Rate 229
  14.5.2 Reaction Rate Constant and the Arrhenius Form 230
  14.5.3 Unimolecular Reactions 230
  14.5.4 More on Reaction Rates 230
  14.5.5 Reaction Mechanisms 230
14.6 Problems 230

Appendices 232
A Physical Constants 232
B Combinatorial Analysis 233
C Tables 234
D Multicomponent, Reactive Flow Conservation Equations 236
E Boltzmann’s Equation 247
F Bibliography for Thermodynamics 252
References 257
Index 261
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>The fundamental problem</td>
</tr>
<tr>
<td>2.1</td>
<td>Interatomic potential energy for the diatomic molecule</td>
</tr>
<tr>
<td>2.2</td>
<td>Thermal equilibrium</td>
</tr>
<tr>
<td>2.3</td>
<td>Mechanical energy reservoir</td>
</tr>
<tr>
<td>2.4</td>
<td>Thermal energy reservoir</td>
</tr>
<tr>
<td>2.5</td>
<td>Graphical illustration of the transformation process</td>
</tr>
<tr>
<td>2.6</td>
<td>Constant-temperature work</td>
</tr>
<tr>
<td>2.7</td>
<td>Joule–Thompson coefficient for several substances (data from <em>Perry’s Chemical Engineers’ Handbook</em> [8])</td>
</tr>
<tr>
<td>3.1</td>
<td>An ensemble of ensemble members</td>
</tr>
<tr>
<td>3.2</td>
<td>Equilibrium rotational population distribution for CO</td>
</tr>
<tr>
<td>3.3</td>
<td>Expected value of $&lt; N_k &gt;$</td>
</tr>
<tr>
<td>3.4</td>
<td>Expected value of $&lt; N_k &gt;$ for a Bose–Einstein system</td>
</tr>
<tr>
<td>3.5</td>
<td>Expected value of $&lt; N_k &gt;$ for a Fermi–Dirac system</td>
</tr>
<tr>
<td>4.1</td>
<td>Spectral distribution of blackbody radiation</td>
</tr>
<tr>
<td>4.2</td>
<td>Photoelectric emission</td>
</tr>
<tr>
<td>4.3</td>
<td>The Compton effect</td>
</tr>
<tr>
<td>4.4</td>
<td>A wave packet</td>
</tr>
<tr>
<td>4.5</td>
<td>The particle in a box</td>
</tr>
<tr>
<td>4.6</td>
<td>Spherical coordinate system</td>
</tr>
<tr>
<td>4.7</td>
<td>The hydrogenic atom</td>
</tr>
<tr>
<td>4.8</td>
<td>Hydrogen atom energy levels</td>
</tr>
<tr>
<td>4.9</td>
<td>Morse and harmonic potentials</td>
</tr>
<tr>
<td>4.10</td>
<td>Rotational motion of a diatomic molecule</td>
</tr>
<tr>
<td>4.11</td>
<td>Vibrational motion of a diatomic molecule</td>
</tr>
<tr>
<td>4.12</td>
<td>Rotational and vibrational energy levels for a diatomic molecule</td>
</tr>
<tr>
<td>4.13</td>
<td>Fine structure splitting for a hydrogenic atom (Incropera [7])</td>
</tr>
<tr>
<td>4.14</td>
<td>The periodic table</td>
</tr>
<tr>
<td>4.15</td>
<td>Sodium energy-level diagram</td>
</tr>
<tr>
<td>4.16</td>
<td>OH energy-level diagram (from Radzig and Smirov [9])</td>
</tr>
<tr>
<td>4.17</td>
<td>Predicted structure of CH$_2$</td>
</tr>
<tr>
<td>5.1</td>
<td>The Maxwellian speed distribution</td>
</tr>
<tr>
<td>5.2</td>
<td>Electronic partition function for Li</td>
</tr>
<tr>
<td>5.3</td>
<td>Equilibrium rotational population distribution for CO</td>
</tr>
</tbody>
</table>
List of Figures

5.4 Effect of number of terms on the value of \(q_r\). Horizontal lines are the high-temperature limit. Although not plotted, the Euler–MacLaurin series converges in only a few terms 101
5.5 Effect of number of terms on error using the high-temperature limit 102
5.6 Typical potential energy function 103
5.7 \(c_v/k\) as a function of temperature for CO 104
6.1 Adiabatic mixing at constant total volume 111
7.1 Spectral distribution of blackbody radiation 124
7.2 Electron energy distribution in a metal matrix 127
7.3 Electron energy distribution 127
7.4 Specific heat as a function of temperature 129
8.1 Rigid sphere, square well, Sutherland (weakly attractive sphere), and Lennard–Jones potential functions (clockwise around figure) 137
9.1 Radial distribution function for crystal structures 146
9.2 Radial distribution function for liquids 146
9.3 Water molecules in simulation box 153
9.4 Radial distribution function 154
10.1 Crystal structure in 2D 157
10.2 The dependence of average potential energy (per atom) on position 157
10.3 Properties of the Einstein crystal 159
10.4 Frequency distributions for Einstein and Debye models 161
10.5 Specific heat for Einstein and Debye models (data from Kittel [10] and White and Collocott [11]) 162
11.1 The fundamental relation 167
11.2 Example fundamental relation 168
11.3 Isotherms of typical \(pvT\) relationship 169
11.4 Single isotherms of typical \(pvT\) relationship 170
11.5 Gibbs potential as a function of \(p\) 171
11.6 Phase diagram for simple compressible substance 171
11.7 Isotherm of typical \(pv\) diagram 172
11.8 Van der Waals equation 172
11.9 Global versus local stability 175
12.1 Relationship between Knudsen number and mathematical models (adapted from Bird [12]) 180
12.2 Gradient Transport 181
12.3 The sphere of influence 182
12.4 Random path of colliding particle 183
12.5 Straightened path of colliding particle 183
12.6 Viscosity of several gases 185
12.7 Viscosity of helium 189
12.8 Thermal conductivity of helium 190
12.9 Self-diffusion coefficient of helium 192
13.1 The Einstein radiative processes 197
13.2 Spectral line shape functions 201
List of Figures

13.3 Sodium energy-level diagram 202
13.4 Rotational absorption spectrum 204
13.5 Vibrational/rotational absorption spectrum (horizontal axis is wavelength) (note that the $J'$ to $J''$ transition that is shown dashed is forbidden; also, the rotational spacings are greatly exaggerated) 205
13.6 Illustration of the Franck–Condon principle 206
13.7 Electronic transitions resulting in a band spectrum. In this case, only $\Delta v = 0$ is allowed. The band locations and shapes depend on the detailed energy-level parameters. The $\Delta v = 0$ bands will overlap if the higher-order terms in $G(v)$ are zero 207
13.8 LIF optical arrangement 210
13.9 Two-level system showing radiative and collisional rate terms 210
13.10 Rayleigh and Raman scattering processes 212
13.11 The Einstein radiative processes 213
14.1 Potential energy barrier 218
14.2 Reaction probability as a function of collision energy 219
14.3 Collision geometry 219
14.4 Acetaldehyde unimolecular decomposition rate constant $k_{uni}$ at 1500 K 223
14.5 $H_2/O_2$ explosion behavior 228
14.6 Temperature, $H_2$, $O_2$, and $H_2O$ vs. time 229
14.7 $H_2O_2$, $HO_2$, H, and O vs. time 229
D.1 Conservation balance 238
D.2 Geometry for calculating number flux 240
D.3 Mass conservation balance 242
E.1 Phase space 248
E.2 Flux in physical space 248
E.3 Flux in velocity space 248
List of Tables

1.1 Characteristic times of transport processes ................................................ page 5
2.1 Equations of state ......................................................................................... 18
2.2 Transformations of the energy representation ................................................. 25
2.3 Transformations of the entropy representation ............................................... 25
3.1 Types of ensembles ....................................................................................... 41
3.2 Types of partition functions ........................................................................ 44
4.1 Degeneracy of translational quantum states ............................................... 68
4.2 Electronic energy levels of sodium ............................................................... 83
4.3 Methods of molecular modeling ................................................................. 86
4.4 Molecular modeling software ..................................................................... 87
4.5 Simple solutions of the wave equation ....................................................... 89
6.1 Mole fractions predicted by Matlab script ................................................... 116
7.1 Electronic properties of metals ................................................................... 126
10.1 Debye temperatures for some monatomic crystalline solids ....................... 163
11.1 Number of phases for a two-component system ......................................... 174
12.1 Non-dimensional parameters of fluid flow ............................................... 179
13.1 Main transition bands ............................................................................... 206
14.1 Detailed H₂/O₂ reaction mechanism (Li et al. [13]) ................................... 227
14.2 Rate constant in units of cm³/molecule sec and temperature in K ............. 231
D.1 Forms of the densities ............................................................................... 239
E.1 Lennard–Jones 6,12 collision integrals (from Hirschfelder, Curtiss, and Bird [14]; also in Bird, Stewart, and Lightfoot [15]) ......................... 250
Preface

I have been teaching advanced thermodynamics for over 40 years, first at the University of California at Berkeley from 1975 through 1988, and since then at the University of Colorado at Boulder. I have mostly had mechanical and aerospace engineering students who are moving toward a career in the thermal sciences, but also a goodly number of students from other engineering and scientific disciplines. While working on my Master’s degree at the University of Michigan I took statistical thermodynamics from Professor Richard Sonntag using his and Gordon Van Wylen’s text *Fundamentals of Statistical Thermodynamics* [1]. Later at Stanford I took Charles Kruger’s course using *Introduction to Physical Gas Dynamics* by Vincenti and Kruger [2]. This course had a large dose of statistical thermodynamics combined with gas dynamics.

Both experiences sharpened my interest in the subject matter. Then, early in my teaching career, I had the good fortune to be introduced to the wonderful text *Thermodynamics and an Introduction to Thermostatistics* by Professor Herbert B. Callen [3] of the University of Pennsylvania. My first reading of his postulatory approach to classical thermodynamics was one of the most exciting learning experiences of my career. As one epiphany followed another, I realized that here was a teacher’s dream, the opportunity to teach classical thermodynamics in a way that makes Gibbs’ [4] ensemble approach to statistical thermodynamics transparent. I have therefore taught advanced thermodynamics in this fashion over the years, but with a serious handicap. There was no available text that was suitable for engineering students and that fully integrates Callen’s postulatory approach with the ensemble approach of statistical mechanics. Eldon Knuth’s book *Introduction to Statistical Thermodynamics* [5] is a good companion to Callen, but uses different notation. Tien and Lienhard’s *Statistical Thermodynamics* [6] introduces the postulatory approach, but in a very short first chapter. They also spend a great deal of time on classical statistics, which I feel is unnecessary when ensemble statistics are used. All are quite dated, especially in terms of advances in computation techniques and modern property compilations. I also feel indebted to Frank Incropera’s book *Introduction to Molecular Structure and Thermodynamics* [7], which provides a particularly easy to follow presentation of quantum mechanics suitable for engineering students.

Hence this book. It assumes the reader is a mechanical or aerospace engineering graduate student who already has a strong background in undergraduate engineering thermodynamics and is ready to tackle the underlying fundamentals of the subject. It is designed for those entering advanced fields such as combustion, high-temperature gas dynamics, environmental sciences, or materials processing, or who wish to build a
background for understanding advanced experimental diagnostic techniques in these or similar fields. The presentation of the subject is quite different from that encountered in engineering thermodynamics courses, where little fundamental explanation is given and the student is required to accept concepts such as entropy and the 2nd Law. Here, the underlying meaning of entropy, temperature, and other thermodynamic concepts will be definitively explored, quantum mechanics learned, and the physical basis of gas, liquid, and solid phases established. In addition, the molecular basis of transport phenomena and chemical kinetics will be explored. Modern tools for solving thermodynamic problems will also be explored, and the student is assured that he or she will gain knowledge of practical usefulness.
Comment on Software

In a number of locations throughout the text, various software programs will be mentioned. Some are open source, others commercial. Two packages are mentioned multiple times: Mathcad and Mathematica. Both are commercial but almost all universities have site licenses for engineering students and student licenses are very affordable. At the University of Colorado we have favored Matlab for many years, and it is expected that students will be adept in its usage. Where other commercial programs are mentioned, there is almost always an open source alternative given as well. As is usually the case, the commercial programs are more polished, with easier to use interfaces. However, the open source programs can work well and in some cases the science is more up to date. I realize that in this day and age electronic anything tends to come and go. I have tried to reference software that is likely to have staying power for some time. However, it is incumbent on any engineer or scientist to stay current on available tools, so I expect that the conscientious student (and teacher) will find suitable alternatives if necessary.
Acknowledgments

In any endeavor such as writing a book of this nature, it is clear that one owes debts to a number of people. My start came from being blessed with being born into an academic family. My father, James W. Daily, studied at Stanford and Cal Tech, before teaching at MIT for 18 years, and later at the University of Michigan, serving as Chair of the Applied Mechanics Department. As a youth I met many giants in engineering and science, including G. I. Taylor, Hermann Schlichting, Theodore von Kármán, and Harold Eugene “Doc” Edgerton. I have already mentioned studying thermodynamics under Richard Sonntag at Michigan. One of my PhD advisors at Stanford was Charles Kruger. I also had classes from Bill Reynolds and Milton Van Dyke, both great minds. And while teaching at Berkeley I had many scintillating conversations with Rick Sherman, Chang Tien, George Pimentel, Yuan Lee, Bill Miller, and Henry “Fritz” Schaefer III. While at Boulder I have developed wonderful collaborations with G. Barney Ellison, John Stanton, Peter Hamlington, Melvin Branch, Greg Rieker, Nicole Labbe, and others. My many colleagues around the world have kept me honest through their reviews of papers and proposals, provided spirited discussions at meetings and meals, and generally challenged me to be my best. And needless to say, my graduate students have provided great joy as we transition from teacher–student into lifelong equals and friends.

At home my wife Carol has been an inspiration. As I write this she is battling ovarian cancer with courage and grace. I am not surprised. She raised four children while working as a teacher and psychotherapist helping children, all while managing to ski, backpack, run marathons, and compete in triathlons. We have been rewarded with ten wonderful grandchildren.

Of course, thanks go to the people at Cambridge University Press, including Steven Elliott and Brianda Reyes. One of our current graduate students, Jeff Glusman, was particularly helpful with proofreading and made many valuable suggestions.

To all these people I give my heartfelt thanks. Because of them I have had a great life that has given me the opportunity to write this book.