Nonequilibrium Gas Dynamics and Molecular Simulation

Starting from the behavior of individual atoms and molecules, including their quantum mechanical energy states, Boyd and Schwartzentruber develop the relationships to classical thermodynamics and gas dynamics phenomena using theory and simulation. Kinetic theory is used to relate the motion and collisions of atoms and molecules to classical fluid dynamics. Quantum mechanics is used to determine the allowed energy states that specific atoms and molecules may occupy. Statistical mechanics uses the quantized energy states to describe the classical thermodynamics state of a gas. These three areas are combined in order to study the nonequilibrium processes of internal energy relaxation and chemistry. All of these theoretical ideas are employed in describing the direct simulation Monte Carlo method, a numerical technique for analysis of nonequilibrium gas dynamics that is based on molecular simulation. This book is aimed at graduate students, engineers, and scientists involved in the study of nonequilibrium gas dynamics.

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NONEQUILIBRIUM GAS DYNAMICS AND MOLECULAR SIMULATION

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Contents

List of Illustrations  ix
List of Tables xv
Preface xvii
Acknowledgments xxi

Part I Theory

1 Kinetic Theory 3
1.1 Introduction 3
1.2 Fundamental Concepts 3
  1.2.1 Particle Model 4
  1.2.2 Macroscopic Quantities from Molecular Behavior 6
  1.2.3 Molecular Collisions 12
  1.2.4 Molecular Transport Processes 14
1.3 Kinetic Theory Analysis 20
  1.3.1 Velocity Distribution Function 20
  1.3.2 The Boltzmann Equation 22
  1.3.3 The H-Theorem of Boltzmann 26
  1.3.4 Maxwellian VDF 29
  1.3.5 Equilibrium Collision Properties 35
  1.3.6 Free Molecular Flow onto a Surface 37
  1.3.7 Kinetic-Based Analysis of Nonequilibrium Flow 44
  1.3.8 Free Molecular Flow Analysis 48
1.4 Summary 50
1.5 Problems 51

2 Quantum Mechanics 54
2.1 Introduction 54
2.2 Quantum Mechanics 54
  2.2.1 Heisenberg Uncertainty Principle 56
  2.2.2 The Schrödinger Equation 57
  2.2.3 Solutions of the Schrödinger Equation 60
## Contents

### 2.2 Two-Particle System
- 2.2.4 Two-Particle System: 62
- 2.2.5 Rotational and Vibrational Energy: 65
- 2.2.6 Electronic Energy: 68

### 2.3 Atomic Structure
- 2.3.1 Electron Classification: 69
- 2.3.2 Angular Momentum: 69
- 2.3.3 Spectroscopic Term Classification: 71
- 2.3.4 Excited States: 72

### 2.4 Structure of Diatomic Molecules
- 2.4.1 Born–Oppenheimer Approximation: 74
- 2.4.2 Rotational and Vibrational Energy: 77
- 2.4.3 Electronic States: 78

### 2.5 Summary: 81

### 2.6 Problems: 82

### 3 Statistical Mechanics

#### Introduction: 84

#### 3.2 Molecular Statistical Methods
- 3.2.1 Energy Groups: 87

#### 3.3 Distribution of Energy States
- 3.3.1 Boltzmann Limit: 92
- 3.3.2 Boltzmann Energy Distribution: 94

#### 3.4 Relation to Thermodynamics
- 3.4.1 Boltzmann's Relation: 97
- 3.4.2 Macroscopic Thermodynamic Properties: 98

#### 3.5 Partition Functions
- 3.5.1 Translational Energy: 99
- 3.5.2 Internal Structure: 103
- 3.5.3 Monatomic Gas: 104
- 3.5.4 Diatomic Gas: 107

#### 3.6 Dissociation–Recombination System: 111

#### 3.7 Summary: 114

#### 3.8 Problems: 114

### 4 Finite-Rate Processes

#### Introduction: 118

#### 4.2 Equilibrium Processes
- 4.2.1 Vibrational Energy: 119
- 4.2.2 Equilibrium Chemistry: 121
- 4.2.3 Equilibrium Constant: 124
- 4.2.4 Equilibrium Composition: 124

#### 4.3 Vibrational Relaxation
- 4.3.1 Vibrational Relaxation Time: 127

#### 4.4 Finite-Rate Chemistry
- 4.4.1 Rate Coefficient: 133
## Contents

4.4.2 Effects of Internal Energy 136  
4.4.3 Calculation of Dissociation Rates 138  
4.4.4 Finite-Rate Relaxation 140  
4.5 Summary 144  
4.6 Problems 144  

## Part II Numerical Simulation

5 Relations Between Molecular and Continuum Gas Dynamics 149  
5.1 Introduction 149  
5.2 The Conservation Equations 150  
5.3 Chapman–Enskog Analysis and Transport Properties 155  
5.3.1 Analysis for the BGK Equation 156  
5.3.2 Analysis for the Boltzmann equation 162  
5.3.3 Analysis for Gas Mixtures 165  
5.3.4 General Transport Properties of Polyatomic Mixtures 168  
5.4 Evaluation of Collision Cross Sections and Transport Properties 173  
5.4.1 Collision Cross Sections 173  
5.4.2 Hard-Sphere Interactions 175  
5.4.3 Inverse Power-Law Interactions 176  
5.4.4 General Interatomic Potentials 178  
5.5 Summary 181  

6 Direct Simulation Monte Carlo 183  
6.1 Introduction 183  
6.2 DSMC Basics 188  
6.2.1 Fundamentals 188  
6.2.2 Particle Movement and Sorting 193  
6.2.3 Collision Rate 197  
6.2.4 Cell and Particle Properties 202  
6.3 Models for Viscosity, Diffusivity, and Thermal Conductivity 204  
6.3.1 The Variable Hard-Sphere Model 204  
6.3.2 The Variable Soft-Sphere Model 216  
6.3.3 Generalized Hard-Sphere, Soft-Sphere, and LJ Models 218  
6.3.4 Thermal Conductivity 224  
6.3.5 Model Parametrization 225  
6.4 Internal Energy Transfer Modeling in DSMC 226  
6.4.1 Continuum and Molecular Models 226  
6.4.2 Post-collision Energy Redistribution 228  
6.4.3 Inelastic Collision Pair Selection Procedures 236  
6.4.4 Generalized Post-collision Energy Redistribution 244  
6.5 Summary 250
# Contents

7 Models for Nonequilibrium Thermochemistry 252

7.1 Introduction 252

7.2 Rotational Energy Exchange Models 252

7.2.1 Constant Collision Number 253

7.2.2 The Parker Model 253

7.2.3 Variable Probability Exchange Model of Boyd 254

7.2.4 Nonequilibrium Direction Dependent Model 255

7.2.5 Model Results 256

7.3 Vibrational Energy Exchange Models 259

7.3.1 Constant Collision Number 259

7.3.2 The Millikan–White Model 260

7.3.3 Quantized Treatment for Vibration 263

7.3.4 Model Results 265

7.4 Dissociation Chemical Reactions 267

7.4.1 Total Collision Energy Model 267

7.4.2 Redistribution of Energy Following a Dissociation Reaction 273

7.4.3 Vibrationally Favored Dissociation Model 276

7.5 General Chemical Reactions 277

7.5.1 Reaction Rates and Equilibrium Constant 277

7.5.2 Backward Reaction Rates in DSMC 281

7.5.3 Three-Body Recombination Reactions 287

7.5.4 Post-Reaction Energy Redistribution and General Implementation 289

7.5.5 DSMC Solutions for Reacting Flows 293

7.6 Summary 309

Appendix A Generating Particle Properties 311

Appendix B Collisional Quantities 323

Appendix C Determining Post-Collision Velocities 329

Appendix D Macroscopic Properties 338

Appendix E Common Integrals 346

References 349

Index 357
<table>
<thead>
<tr>
<th>Illustrations</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Macroscopic and molecular views of a gas at rest</td>
<td>4</td>
</tr>
<tr>
<td>1.2 Interaction potential for two argon particles</td>
<td>5</td>
</tr>
<tr>
<td>1.3 Hard-sphere interaction potential for two argon particles</td>
<td>6</td>
</tr>
<tr>
<td>1.4 Inverse power law interaction potential for two argon particles</td>
<td>7</td>
</tr>
<tr>
<td>1.5 A particle undergoing specular reflection from a wall</td>
<td>8</td>
</tr>
<tr>
<td>1.6 Trajectory of a typical particle</td>
<td>9</td>
</tr>
<tr>
<td>1.7 Sphere of influence for the collision of two like particles</td>
<td>12</td>
</tr>
<tr>
<td>1.8 Actual path of the particle</td>
<td>13</td>
</tr>
<tr>
<td>1.9 Simplified path of the particle</td>
<td>13</td>
</tr>
<tr>
<td>1.10 Collisional merging of two different VDFs</td>
<td>15</td>
</tr>
<tr>
<td>1.11 Assumed situation for analysis of transport properties</td>
<td>16</td>
</tr>
<tr>
<td>1.12 Illustration of how the particle velocity component in $r_2$ affects transport of translational energy</td>
<td>19</td>
</tr>
<tr>
<td>1.13 Volume element in velocity space</td>
<td>21</td>
</tr>
<tr>
<td>1.14 Particle scattering in an intermolecular collision</td>
<td>24</td>
</tr>
<tr>
<td>1.15 Variation of Boltzmann's H-function with time</td>
<td>29</td>
</tr>
<tr>
<td>1.16 Maxwellian VDF in one dimension</td>
<td>33</td>
</tr>
<tr>
<td>1.17 Maxwellian speed distribution</td>
<td>34</td>
</tr>
<tr>
<td>1.18 Coordinate system for particle fluxes</td>
<td>38</td>
</tr>
<tr>
<td>1.19 Free molecular analysis of the surface properties of the Sputnik spacecraft: (a) pressure coefficient; (b) heat flux</td>
<td>43</td>
</tr>
<tr>
<td>1.20 Aerodynamic forces on a surface element</td>
<td>44</td>
</tr>
<tr>
<td>1.21 Collisionless jet expansion: profiles of (a) number density and (b) velocity</td>
<td>50</td>
</tr>
<tr>
<td>2.1 Wave packet representation of particle behavior</td>
<td>55</td>
</tr>
<tr>
<td>2.2 Thought experiment for measurement of particle properties</td>
<td>56</td>
</tr>
<tr>
<td>2.3 Two-particle coordinate system</td>
<td>63</td>
</tr>
<tr>
<td>2.4 Rotations and vibrations of a diatomic particle</td>
<td>65</td>
</tr>
<tr>
<td>2.5 Quantized vibrational energy levels for the harmonic oscillator model</td>
<td>67</td>
</tr>
<tr>
<td>2.6 Portion of the nitrogen atom energy spectrum showing fine structure</td>
<td>71</td>
</tr>
<tr>
<td>2.7 Energy level diagram for atomic nitrogen</td>
<td>73</td>
</tr>
<tr>
<td>Illustrations</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.8 Comparison of atomic and molecular electronic states</td>
<td>75</td>
</tr>
<tr>
<td>2.9 Schematic of the ground electronic potential function</td>
<td>75</td>
</tr>
<tr>
<td>2.10 Illustration of ground and first electronically excited molecular states</td>
<td>76</td>
</tr>
<tr>
<td>2.11 Schematic diagram of ro-vibrational levels</td>
<td>79</td>
</tr>
<tr>
<td>2.12 Potential energy diagram for the three lowest lying electronic states of molecular nitrogen</td>
<td>80</td>
</tr>
<tr>
<td>3.1 Cartesian space for the translational quantum numbers</td>
<td>86</td>
</tr>
<tr>
<td>3.2 Energy group structure</td>
<td>87</td>
</tr>
<tr>
<td>3.3 Illustration of different macrostates</td>
<td>87</td>
</tr>
<tr>
<td>3.4 Counting of microstates using Bose–Einstein statistics</td>
<td>89</td>
</tr>
<tr>
<td>3.5 Counting of microstates using Fermi–Dirac statistics</td>
<td>89</td>
</tr>
<tr>
<td>3.6 Isothermal expansion of a gas into a vacuum</td>
<td>96</td>
</tr>
<tr>
<td>3.7 Translational energy distribution function</td>
<td>100</td>
</tr>
<tr>
<td>3.8 Electronic specific heat as a function of temperature</td>
<td>106</td>
</tr>
<tr>
<td>3.9 Number of vibrational degrees of freedom as a function of temperature</td>
<td>110</td>
</tr>
<tr>
<td>3.10 Relative energies of atoms and molecules</td>
<td>112</td>
</tr>
<tr>
<td>4.1 Specific internal energies as a function of temperature for N₂</td>
<td>120</td>
</tr>
<tr>
<td>4.2 Vibrational energy distributions for N₂</td>
<td>120</td>
</tr>
<tr>
<td>4.3 Characteristic density for dissociation of N₂</td>
<td>123</td>
</tr>
<tr>
<td>4.4 Equilibrium degree of dissociation</td>
<td>123</td>
</tr>
<tr>
<td>4.5 Equilibrium composition of air (a) at 1 atm; (b) at 0.01 atm</td>
<td>125</td>
</tr>
<tr>
<td>4.6 Vibrational relaxation in a heat bath</td>
<td>127</td>
</tr>
<tr>
<td>4.7 Vibrational and rotational collision numbers for air molecules</td>
<td>128</td>
</tr>
<tr>
<td>4.8 Equilibrium constant for nitrogen dissociation–recombination</td>
<td>132</td>
</tr>
<tr>
<td>4.9 Nitrogen dissociation rate as a function of temperature</td>
<td>133</td>
</tr>
<tr>
<td>4.10 Effect of collision orientation on reaction likelihood</td>
<td>134</td>
</tr>
<tr>
<td>4.11 Illustration of the line of centers of a collision</td>
<td>135</td>
</tr>
<tr>
<td>4.12 NO–NO dissociation rates as a function of temperature</td>
<td>140</td>
</tr>
<tr>
<td>4.13 Species mass fractions as a function of time for the (N₂, N) system for a fixed temperature</td>
<td>141</td>
</tr>
<tr>
<td>4.14 Species mass fractions and temperature as a function of time for the (N₂, N) system</td>
<td>142</td>
</tr>
<tr>
<td>4.15 Species mole fractions as a function of time for air at fixed temperature</td>
<td>143</td>
</tr>
<tr>
<td>5.1 Various numerical methods and associated model parameters</td>
<td>150</td>
</tr>
<tr>
<td>5.2 Momentum transfer due to thermal molecular motion relative to the bulk flow velocity</td>
<td>152</td>
</tr>
<tr>
<td>5.3 Viscosity and momentum cross sections and collision integrals for Lennard–Jones and inverse power law potential energy functions</td>
<td>178</td>
</tr>
<tr>
<td>6.1 Gas flow regimes and implications for physical models</td>
<td>184</td>
</tr>
</tbody>
</table>
6.2 Schematic of the underlying characteristics of the DSMC method
6.3 Schematic of DSMC simulation particles within collision cells and sampled distribution function
6.4 Examples of flow field grids used in DSMC implementations
6.5 Particle tracking procedures relevant to the DSMC method
6.6 Instantaneous collision rate and temperature computed for a uniform, equilibrium, argon gas. Symbols represent quantities calculated at each timestep and lines represent time averaged quantities. Circles and solid line refer to the collision rate fraction. Triangles and dashed line refer to the gas temperature
6.7 Normalized density profiles in a Mach 9 argon shock wave
6.8 Distribution functions for $x$-velocity within a normal shock wave in argon
6.9 Normalized He and Xe profiles for a Mach 3.61 normal shock wave (1.5% Xe and 98.5% He) predicted by DSMC and pure MD simulation
6.10 Binary viscosity and diffusion coefficients, for He–Xe interactions, corresponding to various models
6.11 Viscosity and momentum cross sections corresponding to the VSS model, in function of $\alpha$
6.12 Viscosity coefficients for argon corresponding to various models
6.13 Density and temperature profiles within the shock wave
6.14 The process to select an inelastic collision using selection procedure (C). In the figure, $R_n (n = 1, 2, 3, 4)$ are uniform random numbers between 0 and 1, and $P_{\text{rot},i}, P_{\text{vib},i} (i = 1 \text{ or } 2)$ are the rotational and vibrational inelastic collision probabilities used in DSMC for particle $i$
6.15 Rotational and vibrational relaxation temperature histories in an isothermal reservoir
6.16 Comparison of two different selection procedures for rotational relaxation in a two species mixture in an isothermal reservoir simulation
7.1 Experimental and computational data for the rotational collision number
7.2 Rotational relaxation for different models
7.3 Temperature dependence of the vibrational relaxation time constant $\tau_{\text{vib}}$ and collision number $Z_{\text{vib}}$
7.4 Rotational and vibrational excitation using various models
7.5 Dissociation probability as a function of collision energy for various model parameter values
7.6 Schematic showing the procedure to determine post-collision energies following a dissociation reaction 273
7.7 Comparison of existing experimental dissociation rate coefficients for N₂ 279
7.8 The left-hand side of Eq. 7.57 for reactions 4 and 5 as a function of temperature 282
7.9 Backward reaction rates for the Zeldovich exchange reaction, involving O₂ + N, as a function of temperature 284
7.10 Backward reaction rates for the Zeldovich exchange reaction, involving NO + N, as a function of temperature 284
7.11 Equilibrium composition as a function of temperature when only the Zeldovich exchange reactions are included. Plotting scheme: solid line = forward rates from Table 7.2 and backward rates evaluated from accurate equilibrium constants; dashed line = rates from Table 7.3. ◦ = N₂, ∆ = O₂, ∇ = N, ◊ = O, ◳ = NO 286
7.12 Schematic showing the procedure to determine post-collision energies following an exchange reaction 289
7.13 Schematic showing the procedure to determine post-collision energies following a recombination reaction 289
7.14 Isothermal relaxation of nitrogen to T_tr = 6500 K 296
7.15 Isothermal relaxation of nitrogen to T_tr = 13,000 K showing system temperatures and composition 297
7.16 Isothermal relaxation of nitrogen to T_tr = 20,000 K showing system temperatures and composition 298
7.17 Adiabatic relaxation of nitrogen, initialized with T_tr = 13,000 K and T_rot = T_vib = 200 K 299
7.18 Adiabatic relaxation of nitrogen, initialized with T_tr = 20,000 K and T_rot = T_vib = 200 K 300
7.19 Isothermal relaxation of air to T_tr = 6500 K 301
7.20 Isothermal relaxation of air to T_tr = 13,000 K 303
7.21 Isothermal relaxation of air to T_tr = 20,000 K 304
7.22 Contours of translational temperature for Mach 12 nitrogen flow over a 8 cm diameter cylinder at 70 km altitude. Chemical reactions are not considered 305
7.23 Stagnation line profiles for non-reacting nitrogen flow over a cylinder 306
7.24 Stagnation line profiles for dissociating nitrogen flow over a cylinder 307
7.25 Stagnation line temperature profiles in dissociating air flow over a cylinder 308
7.26 Stagnation line profiles for species mass fractions in dissociating air flow over a cylinder 308
Illustrations

A.1 Face-normal coordinate system used to determine particle flux through a planar element and particle properties 318
C.1 Schematic showing the procedure to determine post-collision velocity vectors following a dissociation reaction 333
C.2 Schematic showing the procedure to determine post-collision velocity vectors following an exchange reaction 334
C.3 Schematic showing the procedure to determine post-collision velocity vectors following a recombination reaction 336
## Tables

1.1 Molecular Transport Properties | page 15
2.1 First Few Quantized Translational Energy Levels | 62
2.2 Table of Electron Classification | 70
2.3 Lowest Lying Electronic States of Air Atoms | 72
2.4 Ground State Molecular Constants for the NRR/AHO Model | 78
3.1 Distributions of Particles in Energy States | 85
4.1 Sources of Energy for Nitrogen Dissociation Reactions | 138
5.1 Atomic Parameters | 179
5.2 Mixture Viscosities Computed from LJ Interatomic Potential Parameters | 180
6.1 VHS Model Parameters | 213
6.2 GHS-Weak Model Parameters for Argon | 222
6.3 Simulation Parameters Specific to Each Collision Pair | 243
7.1 Parameter Values for the Millikan–White Vibrational Relaxation Model for Air Species | 261
7.2 Forward Reaction Rate Coefficients (m³/molecule/s) for Five-Species High-Temperature Air | 278
7.3 Backward Reaction Rate Coefficients (m³/molecule/sec) Fit in Modified Arrhenius Form for Possible Use in DSMC | 283
7.4 DSMC Model Parameters for Each Species | 294
7.5 DSMC VHS Model Parameters for Each Species Pair | 294
Preface

There are two top-level goals that we aim to address in this book: (1) to provide a description of a gas by considering its most basic constituents, i.e., atoms and molecules, and (2) to introduce readers to computer simulation techniques that are available to analyze a gas at this fundamental level.

The first question we must ask ourselves is, Why should we consider a gas at the molecular level? After all, there are well-established equations and ideas that provide accurate descriptions of gas flow at the macroscopic level that employ variables such as density, flow velocity, temperature, and pressure, and these represent properties that take into account the molecules in an aggregate sense. Certainly, the molecular approach will provide us with a deeper understanding of all gas flows. However, more than that, under certain conditions, the aggregate, or sometimes called fluid, approach is not able to provide a physically accurate picture of the gas. We will find that these conditions arise when there is either not enough time or physical space for a sufficient number of intermolecular collisions to occur to maintain the gas in the well-understood equilibrium state. We refer to such conditions as nonequilibrium. To describe nonequilibrium flows accurately, we need to study the molecular nature of the gas.

There are a number of important application areas in aerospace engineering where nonequilibrium gas flows arise. In general, we will find that nonequilibrium occurs when the gas flow is at low density and/or involves very small length scales. One important application area for nonequilibrium is the flight of high-speed vehicles at very high altitude in the Earth’s atmosphere. Examples include spacecraft returning from orbit, such as the space shuttle, or hypersonic cruise vehicles. These vehicles have a length scale of several meters, and move at very high speed so that the flow field surrounding them involves very high temperatures. However, it is their operation in the low-density environment of near-space that leads to nonequilibrium gas flow phenomena. We focus on low-density, high-temperature air in many of the examples and analyses presented throughout the book.

A second important technology area involving nonequilibrium gas flow is micro- and nanoelectromechanical systems (MEMS/NEMS) that involve fabrication and operation of very small machines based on microfabrication techniques.
technology. When these devices involve gas flow, the velocities are usually very low and certainly subsonic, and the pressure and temperature are close to atmospheric. In this case, it is the very small length scales, around 1 micron = \(10^{-6}\) m, that may give rise to nonequilibrium gas flow behavior.

A third example of nonequilibrium flow is for small rockets used to maneuver spacecraft when they are in orbit. There are a number of different types of these spacecraft thrusters, but they are generally supersonic, involve relatively low-pressure gas or plasma, and have length scales of a few centimeters. This is a case where it is a combination of low pressure and small length scale that gives rise to nonequilibrium phenomena. The same type of physical situation occurs in related technology areas such as vapor deposition and etching machines employed in the materials processing industry.

Another motivation for considering the molecular properties of gas is that this is required to understand a number of modern optical diagnostics techniques that are used to study gas flows whether they are in a state of equilibrium or not. Examples of such diagnostics include emission spectroscopy and laser-induced fluorescence. These techniques rely on the quantum mechanical energy structure of atoms and molecules to derive basic gas flow information such as density, flow velocity, and temperature.

The book is divided into two parts based on the overall goals, with the first part focusing on fundamental considerations, and the second part dedicated to describing computer simulation methods.

The first section covers three different areas: (1) kinetic theory, (2) quantum mechanics, and (3) statistical mechanics. Important results from these three areas are then brought together to allow analysis of nonequilibrium processes in a gas based on molecular level considerations.

Chapter 1 covers kinetic theory, in which the basic idea is to develop techniques to relate the properties and behavior of particles, representing atoms and molecules, to the fluid mechanical aspects of gas at the macroscopic level. This requires us to provide a basic definition by what is meant by a particle, and how these particles interact with one another through the mechanism of intermolecular collisions. This leads us into a discussion of modeling macroscopic molecular transport processes, such as viscosity and thermal conductivity, that represents one of the first key successes of kinetic theory.

We will find that kinetic theory relies on the use of statistical analysis techniques, such as probability density functions, owing to the very large volumes of information involved in tracking the behavior of every single particle in a real gas flow. We will formulate the governing equation of kinetic theory, the Boltzmann equation, in terms of the velocity distribution function. We will find that general solution of the Boltzmann equation is challenging because of its mathematical properties. However, simple solutions are readily available for equilibrium conditions, and these can be further employed for analysis of the properties at a surface in free molecular flows, ones in which there
are no intermolecular collisions. We also review methods derived from the Boltzmann equation for analysis of nonequilibrium gas flows.

In Chapter 2, we cover the internal energy structure of atoms and molecules. This involves consideration of the basic ideas of quantum mechanics, where once again a statistical modeling approach is required. However, in this case the need for such an approach is dictated by the Heisenberg Uncertainty Principle related to the wavelike properties that particles possess. Through the introduction of a number of fundamental postulates, we derive the governing equation of quantum mechanics, the Schrödinger equation for a number of different cases. Solution of the Schrödinger Equation gives rise to the quantized energy states that specific atoms and molecules are allowed to occupy. Specifically, we find that there are four different energy modes that different particles may acquire: translational, electronic, rotational, and vibrational, with the last two occurring only in molecules. In this chapter, we also study the actual energy structure of atoms and molecules that occur in high-temperature air as we will need this information in later analyses.

Chapter 3 addresses statistical mechanics in which the aim is to relate particle behavior to macroscopic thermodynamics. This connection is established through the Boltzmann relation, which links the random nature of particle behavior to macroscopic entropy. The random nature is quantified by analysis of how particles can be arranged across the quantized energy states available to them. Once again, a statistical approach is required and this time it is due to the very large number of quantized energy states that we determined in Chapter 2. Two different statistical counting methods are presented, and through analysis we derive partition functions that provide a pathway to classical thermodynamics. We also extend our results to the case of a chemically reacting system for use in later analysis of such phenomena.

Chapter 4 concludes the first part of the book by bringing together ideas from kinetic theory, quantum mechanics, and statistical mechanics in order to analyze finite-rate, nonequilibrium processes. The processes of interest include change in the vibrational energy of a gas and chemical reactions. In each case, these phenomena proceed at the molecular level through intermolecular collisions, and in general require a finite amount of time to reach completion, which is referred to as the equilibrium state. We first consider the limiting case where this state is reached instantaneously, and consider equilibrium results for both vibrational energy and chemical composition. We then analyze these same processes at the molecular level, using results from Chapters 1 to 3, to formulate approaches that allow finite-rate, nonequilibrium analysis of vibrational and chemical relaxation.

The second part of the book describes computational simulation approaches for the analysis of nonequilibrium gas phenomena that are based on the fundamental ideas presented in Chapters 1 through 4.
Preface

In Chapter 5 the mathematical connection between the Boltzmann equation and the most commonly used forms of the continuum Navier–Stokes equations is developed in the limit of near-equilibrium flow. In the process, a quantitative measure for the accuracy and applicability of the Navier–Stokes equations under nonequilibrium flow conditions is established. This theory reveals how interatomic forces (the model for molecular dynamics calculations) are related to collision cross sections (the model for direct simulation Monte Carlo [DSMC]), and how these cross sections determine the transport properties for viscosity, thermal conductivity, and diffusivity (the models used in continuum computational fluid dynamics calculations). A main goal of Chapter 5 is to establish the collision cross section as a physically meaningful parameter that becomes the key model parameter for the DSMC method.

Chapter 6 describes, in detail, the DSMC method. DSMC is a stochastic particle simulation method that simulates the Boltzmann equation. The applicable flow regimes for the DSMC method are first outlined. Well-established algorithms for calculating collision rates and collision outcomes are presented. The manner in which these collision models determine the gas viscosity, thermal conductivity, and diffusivity are described and example simulations are presented. DSMC models and algorithms for internal energy exchange are described and consistency with continuum models is analyzed. For nonequilibrium flows without chemical reactions, the computational models and algorithms detailed in Chapter 6 enable accurate simulations of the Boltzmann equation for flows ranging from continuum to free molecular.

Finally, Chapter 7 presents DSMC models and algorithms for nonequilibrium reacting flows. High-temperature reacting flows involve significant rotational and vibrational energy excitation and coupling to chemical reactions. The DSMC collision models detailed in Chapter 7 are well established in terms of their physical accuracy and computational efficiency. We present example DSMC simulations for high-temperature reacting air flows, and discuss the most current research and prospects for future DSMC models required for nonequilibrium reacting flows.

This book grew out of two different graduate-level courses taught by the authors. Part I is based on a course on nonequilibrium molecular gas dynamics that is a core graduate class in aerospace engineering at the University of Michigan. It provides the fundamental background needed to understand Part II that is based on an advanced graduate class on computer simulation of gas dynamics in aerospace engineering at the University of Minnesota. In addition to serving as a textbook for such graduate classes, the contents of the book will be useful for researchers in nonequilibrium gas dynamics to understand the basic physical phenomena, as well as how to analyze such flows using computer simulation.
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