

# Contents

|                       |                |
|-----------------------|----------------|
| List of Illustrations | <i>page</i> ix |
| List of Tables        | xv             |
| Preface               | xvii           |
| Acknowledgments       | xxi            |

## Part I Theory

|  |           |
|--|-----------|
| <b>1 Kinetic Theory</b>                              | <b>3</b>  |
| 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        |
| <b>2 Quantum Mechanics</b>                           | <b>54</b> |
| 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        |

|  |            |
|--|------------|
| 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                       | 69         |
| 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        | 73         |
| 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         |
| <b>3 Statistical Mechanics</b>             | <b>84</b>  |
| 3.1 Introduction                           | 84         |
| 3.2 Molecular Statistical Methods          | 84         |
| 3.2.1 Energy Groups                        | 87         |
| 3.3 Distribution of Energy States          | 90         |
| 3.3.1 Boltzmann Limit                      | 92         |
| 3.3.2 Boltzmann Energy Distribution        | 94         |
| 3.4 Relation to Thermodynamics             | 95         |
| 3.4.1 Boltzmann’s Relation                 | 97         |
| 3.4.2 Macroscopic Thermodynamic Properties | 98         |
| 3.5 Partition Functions                    | 99         |
| 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        |
| <b>4 Finite-Rate Processes</b>             | <b>118</b> |
| 4.1 Introduction                           | 118        |
| 4.2 Equilibrium Processes                  | 119        |
| 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                 | 126        |
| 4.3.1 Vibrational Relaxation Time          | 127        |
| 4.4 Finite-Rate Chemistry                  | 129        |
| 4.4.1 Rate Coefficient                     | 133        |

|       |                                   |     |
|-------|-----------------------------------|-----|
| 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

|          |   |            |
|----------|---|------------|
| <b>5</b> | <b>Relations Between Molecular and Continuum Gas Dynamics</b>   | <b>149</b> |
| 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        |
| <b>6</b> | <b>Direct Simulation Monte Carlo</b>                            | <b>183</b> |
| 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        |

|   |     |
|---|-----|
| <b>7 Models for Nonequilibrium Thermochemistry</b>                      | 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<br>Implementation | 289 |
| 7.5.5 DSMC Solutions for Reacting Flows                                 | 293 |
| 7.6 Summary   | 309 |
| <b>Appendix A Generating Particle Properties</b>                        | 311 |
| <b>Appendix B Collisional Quantities</b>                                | 323 |
| <b>Appendix C Determining Post-Collision Velocities</b>                 | 329 |
| <b>Appendix D Macroscopic Properties</b>                                | 338 |
| <b>Appendix E Common Integrals</b>                                      | 346 |
| References  | 349 |
| Index   | 357 |