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 nonequilbrium 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.

Iain D. Boyd received a doctorate in aeronautics and astronautics from the University of Southampton. He worked at NASA Ames Research Center and Cornell University, before joining the University of Michigan. He has authored more than 200 journal articles and 300 conference papers. Professor Boyd is a Fellow of the American Physical Society and a Fellow of the American Institute of Aeronautics and Astronautics from which he also received the 1998 Lawrence Sperry Award. He has served on the editorial boards of *Physics of Fluids*, *Journal of Spacecraft and Rockets*, *Journal of Thermophysics and Heat Transfer*, and *Physical Review Fluids*.

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NONEQUILIBRIUM GAS DYNAMICS AND MOLECULAR SIMULATION

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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 nonequilibium 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

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 a 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.

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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