Chemically reacting flow is a very broad topic that directly and indirectly touches many aspects of everyday life. Long-standing examples include combustion, chemical synthesis, heterogeneous catalysis, atmospheric chemistry, and materials processing. Emerging examples include electrochemical power sources such as fuel cells. The first objective of this book is to establish the theoretical underpinnings that enable the development of new models. Accomplishing this objective begins with detailed derivations of the fundamental conservation laws of mass, momentum, and energy for chemically reacting, viscous, fluid mechanics (i.e., the Navier–Stokes equations). Of course, the basic conservation equations have been well known for over a century. Moreover, the equations can be solved using modern Computational Fluid Dynamics (CFD) software for geometrically and chemically complex three-dimensional problems.

Inasmuch as the fundamental conservation equations are already well known, the purpose of presenting detailed derivations is not to establish the equations themselves. Rather the intent is to provide the insight and interpretation that help in deriving related systems of equations to model particular problems that can benefit from physical or dimensional approximations or reductions. Although general-purpose CFD software can solve most problems using the full Navier–Stokes equations, the required time and computational expense can be significant. By recognizing and exploiting problem-specific simplifications, simulation time can often be very greatly reduced. In such cases, however, the governing equations may not be readily apparent or available. The systematic approach that is used for
INTRODUCTION

deriving the Navier–Stokes equations establishes a pattern that can be followed in deriving related, but reduced, conservation equations for particular problems.

Beyond initially deriving the full Navier–Stokes equations, the present book is largely concerned with problems that can be formulated and solved in some reduced setting. The most straightforward approach to model reduction is simply dimensional reduction. Recognizing the problem attributes that enable a one- or two-dimensional representation is certainly valuable compared to solving a three-dimensional problem. So-called boundary-layer approximations offer great simplifications, but can be more difficult to recognize and implement. The boundary-layer approximations, as first recognized by Prandtl and colleagues in the early 1900s, are based upon scaling arguments. By neglecting certain terms that can be shown to be small in certain flow regimes, elliptic operators can be replaced by parabolic operators, leading to very great improvements in computational efficiency but with negligible loss of accuracy. Other approaches involve recognizing mathematical similarity, leading to the transformation of partial differential equations to ordinary differential equations and thus great mathematical and computational simplifications. Variations of these approaches are developed via examples throughout the book.

Faced with a new flow configuration or design problem, it can be a challenge to develop a suitably reduced set of governing equations. Indeed, in some cases, reduction may not be possible. Nevertheless, given the computationally intensive task of solving multidimensional chemically reacting flow problems with complex chemistry, there is great benefit to finding appropriate reductions.

1.1 Foregoing Texts

There are certainly foregoing texts that cover material that is similar to the present book. However, the present text differs from earlier offerings in several ways. Most books on fundamental fluid mechanics are not particularly concerned with incorporating heat and multicomponent mass transfer, including chemical reaction. Fluid-mechanics text usually consider aspects of turbulent flow, which is entirely neglected in the present text. Books on combustion certainly consider heat and mass transfer as well as gas-phase chemical reaction. However, most such offerings concentrate on global representations of the chemistry, and usually are not at all concerned with heterogeneous chemistry (e.g., catalysis) at fluid-surface interfaces.

The present book considers only laminar flow, with considerable attention devoted to the details of molecular-transport processes. The applications are generally concerned with internal flows with small spatial dimensions (i.e., low Reynolds numbers). Many chemical reactors (for example, so-called microchannel reactors) fall into this regime. Small-scale heat-exchangers and fuel cells are based on the laminar flow in relatively small channels. Chemical reactors typically rely on catalysts, either in packed beds or as channel washcoats.

The present book is concerned entirely with computational modeling. The conservation equations that govern fundamental fluid mechanics are inherently nonlinear, making exact solutions generally unavailable. There are certainly some fluid-mechanics problems that can be solved exactly, and many texts develop such solutions. Analytic solutions, however, at the least, demand approximations such as constant properties. Once chemistry is
included, exact solutions are essentially impossible. Even in simple flows where analytic solutions are available, the present book develops computational approaches. The intent is to establish the numerical methods and apply simulation software that is needed for more difficult problems. Although alternative computational settings are readily available, the present book uses MATLAB as a convenient and readily available programming environment.

1.2 Objectives and Approach

An engineer or scientist is frequently challenged with the task of developing a simulation to explain an observed physical phenomena or to assist the design and optimization of a system or process. Certainly the task is facilitated significantly by a capability to predict, quantitatively, the outcomes of contemplated alternatives. The objective in this text is to present theory and modeling approaches that facilitate accomplishing this task. The required predictive capability is comprised of several essential elements:

- A system of conservation equations, whose solution describes the velocity, temperature, and composition fields. These equations usually take the form of partial differential equations that are derived from physical laws governing the conservation of mass, momentum, and energy.
- A set of simplifying assumptions that render the system of governing equations solvable with an acceptable level of analytical or computational effort.
- A means to find or estimate required constitutive properties that appear in the conservation equations. These can include equations of state, thermodynamic and transport properties, and chemical reaction rates.
- A means to develop or acquire a chemical reaction mechanism that adequately describes the critical reaction pathways and their rates.
- A method to solve the conservation equations, producing the required velocity, temperature, and composition fields.
- A method to interpret the solutions in terms of design objectives. This task is typically accomplished by evaluating surface fluxes from derivatives of the solution fields (e.g., fluid-mechanical drag based on velocity gradients, material deposition rates based on concentration gradients, and surface heat transfer based on temperature gradients).

1.3 What is a Fluid?

Any material that deforms continuously under the influence of shearing forces is called a fluid. For example, imagine a fluid in an infinitely long annular region between a solid shaft and an outer cylindrical shell. When a torque is applied to the shaft, the shaft will continue to turn as long as the torque is applied and regardless of how small the torque. The shaft’s rotation rate depends on the magnitude of the torque and the properties of the particular fluid. If, instead of a torque, only a normal force is applied (e.g., by an expanding shaft diameter), then the fluid compresses but does not continue to deform. In this hydrostatic situation, in the absence of shear forces, the fluid behaves much the same as a solid. By contrast with a fluid, consider how a solid material would behave if it occupied the annular
space between the shaft and the outer shell. For a given torque on the shaft, the solid would
deform slightly until its resistive force just balances that exerted by shaft and the system
would come to rest in a state of equilibrium shear stress.

Generally speaking, a fluid can be a liquid or a gas, where an important difference is in the
equation of state that provides a quantitative relationship among the pressure, temperature,
and mass density. Gases, of course, are compressible; in the simplest case an ideal gas law
provides the equation of state for a multicomponent mixture as

$$\rho = \frac{p}{RT} \bar{W} = \frac{p}{RT} \sum_{k=1}^{K_g} X_k W_k, \quad (1.1)$$

where $\rho$ is the mass density, $p$ is the thermodynamic pressure, $R$ is the universal gas con-
stant, $\bar{W}$ is the mean molecular weight, $X_k$ is the mole fraction of the $k$th chemical con-
stituent in multicomponent mixture, $W_k$ is the molecular weight of the $k$th component, and
$K_g$ is the total number of gas-phase species. While the material in this book is concerned
primarily with ideal-gas mixtures, other non-ideal equations of state may be appropriate for
high-pressure gases. Liquids are more likely to be approximated as incompressible, where
the mass density $\rho$ is a constant, independent of pressure and temperature. At sufficiently
high pressure and temperature, fluids become supercritical, where the distinction between
a liquid and gas is blurred and an non-ideal equation of state is required.

In addition to the equation of state, it is necessary to describe other thermodynamic
properties of the fluid. These include specific heat, enthalpy, entropy, and free energy.
For ideal gases the thermodynamic properties usually depend on temperature and mixture
composition, with negligible pressure dependence. Most descriptions of fluid behavior
also depend on transport properties, including viscosity, thermal conductivity, and diffu-
sion coefficients. These properties generally depend on temperature, pressure, and mixture
composition.

This book considers only fluids that are isotropic, meaning that the fluid properties are
independent of direction. Such fluids are known as Newtonian fluids. By contrast, solids
can readily have spatially oriented properties. Consider, for example, a common material
like graphite, whose molecular structure has strongly oriented layers. Both mechanical and
thermal properties are vastly different normal to and parallel to the layers. While ordinary
fluids exhibit no such properties, it is possible to have anisotropic fluids. For example, long-
chain polymeric fluids can exhibit properties that are oriented relative to the flow directions.

1.3.1 Continuum Velocity

Velocity is a relatively simple and intuitive concept for a solid body. Because a fluid is con-
tinuously deformable, however, defining its velocity takes a bit more care. At the smallest
scale the fluid is an ensemble of molecules. In principle, one can describe the velocity of
a fluid in terms of the velocities of each molecule in the fluid. Obviously, this would be
impractical owing to the extreme numbers of molecules that would have to be considered.
Instead, it is appropriate to use a velocity field that represents an average fluid velocity at
every point within a macroscopic fluid domain.
Consider a “packet” of fluid whose size is small compared to the length scales over which the macroscopic velocity varies in a particular flow situation, yet large compared to molecular scales. Consider air at room temperature and atmospheric pressure. Using the ideal-gas equation of state, it is easily determined that there are approximately $2.5 \times 10^7$ molecules in a cube that measures 1 μm on each side. For a typical fluid-mechanics problem, velocity fields rarely need to be resolved to dimensions as small as a micrometer. Yet, there are an enormous number of molecules within such a small volume. Consequently, representing the fluid velocity as continuum field using an average of the molecular velocities is an excellent approximation.

From basic statistical-thermodynamics arguments [1], the mean molecular speed in a gas can be determined approximately from the relationship between pressure and mass density as

$$p = \frac{1}{3} \rho \langle V^2 \rangle,$$

where $\langle V^2 \rangle$ is the ensemble average of the square of the molecular velocities. Again, considering air at room temperature and atmospheric pressure, the mean molecular speed is approximately 450 m s$^{-1}$—a large number compared to the fluid velocities in many practical flow problems. Since the molecular motion is randomly directed and the number of molecules in a fluid packet is very large, the molecular velocities do not usually contribute directly to the net fluid velocity. Instead, the effect of the molecular motion is felt in terms of the internal energy of the fluid. For a gas, the molecular velocity and the temperature are related as

$$\frac{1}{2} m \langle V^2 \rangle = \frac{3}{2} k_B T,$$

where $m$ is the mass of an individual molecule and $k_B = 1.38 \times 10^{-23}$ J molecule$^{-1}$ K$^{-1}$ is the Boltzmann constant.

Within the scope of the present book (i.e., continuum fluid mechanics), the focus is on the macroscopic fluid velocities. Molecular-scale velocities are considered only indirectly inasmuch as they affect the equations of state (Chapter 2), thermodynamic properties (Chapter 10), and transport properties (Chapter 11).

Another aspect of relevant velocity scales is concerned with reference frames. Consider, for example, the flow of coolant water within an automotive internal combustion engine system. The relevant reference frame is the automobile, regardless of whether the car is moving or not. The earth is spinning, which affects velocities in the reference frame of the universe. Clearly, one does not consider analyzing the automotive cooling system in the reference frame of the universe.

### 1.3.2 Mean-Free Path

Molecules in a gas are in constant vibrational, rotational, and translational motion. Although certainly very small, molecules have a nonzero diameter, leading to molecular collisions. As a molecule translates some distance $l$ through space, it effectively sweeps out a (cylindrical) volume in a given time proportional to the molecular diameter squared, $V = \pi d^2 l$. (A rigorous derivation taking into account the fact that all of the other molecules in the gas are also moving increases this volume by a factor of $\sqrt{2}$; see Chapter 11.) Any
Processes such as chemical vapor deposition must sometimes consider the effects of submicron features at the deposition surfaces. When the features sizes are on the order of the mean-free-path length, then continuum assumptions can be questionable.

Figure 1.1  Processes such as chemical vapor deposition must sometimes consider the effects of submicron features at the deposition surfaces. When the features sizes are on the order of the mean-free-path length, then continuum assumptions can be questionable.

other molecule whose center lies within in this volume will undergo a collision. Thus, the number of collisions in that given time equals the number of molecules within that volume, \( nV \), where \( n \) is the number density of molecules, which may be evaluated from an equation of state. The average distance that a molecule travels before suffering a collision is called the mean-free path and is just the length traveled divided by the number of collisions

\[
L = \frac{l}{\sqrt{2\pi d^2 \ln n}}. \tag{1.4}
\]

Substituting all of the relevant constants and applying the ideal gas law yields \( L \) (meters) as

\[
L = \frac{T}{d^2 p} \times 3.067 \times 10^{-29}, \tag{1.5}
\]

where \( T \) is the temperature (Kelvins), \( p \) is the pressure (atmospheres), and \( d \) is the molecular diameter (meters). Molecular diameters are typically of the order of a few times \( 10^{-10} \) meters; for example, with gas-phase nitrogen \( d_{N_2} = 3.74 \times 10^{-10} \) m. Thus, at 298 K and 1 atm, the mean distance between collisions for nitrogen is \( 6.62 \times 10^{-8} \) m. Such a distance is very small compared to the size of a control volume in many applications of fluid flow modeling, and the continuum approximation is excellent. However, the mean-free path scales inversely with pressure. If one is interested in modeling dimensions on the scale of microelectronic features in the \( 10^{-6} \) m range, and the pressure is reduced below atmospheric by three orders of magnitude (not uncommon for plasma processing applications), the mean-free path is greater than the feature scale of interest. In this application, considering the gas to be a continuous fluid would be a poor approximation. Thus, it is always good to keep in mind such length-scale arguments. The usual way of quantifying the continuum approximation is through the Knudsen number, \( Kn \), which is the ratio of the mean-free path length to a relevant characteristic length scale. When \( Kn < 0.1 \), the continuum approximation is usually valid.
1.3.3 Range of Scales

The length scales over which fluid packets can be approximated as a continuum vary greatly from application to application. Weather patterns or ocean currents usually represent the largest scales of interest. Here fluid packets, perhaps represented as finite-element grids, can be as large as kilometers. Only in the upper reaches of the atmosphere, where the mean-free-path length between molecular collisions becomes great due to near-vacuum conditions, does the continuum assumption begin to break down. In chemical processes, such as the chemical-vapor-deposition (CVD) reactor shown in Fig. 1.1, the length-scale of interest is typically centimeters. At atmospheric pressure and at reduced pressures of tens of millibars, the continuum approximation is excellent. Some plasma processes, however, operate at a few microbars. In these cases, as the mean-free paths become long, the flows begin to experience non-continuum behaviors. Another place that non-continuum effects can play a role is in the vicinity of small features on surfaces. For example, as illustrated in Fig. 1.1, semiconductor-fabrication processes must contend with filling or etching sub-micron trenches or vias. Even at moderate reactor pressures, the mean-free-path length can approach the dimensions of the feature. In these cases, while the mean flow at the reactor scale is fully continuum, the surface boundary conditions may have to account for non-continuum behavior.

As the Knudsen number increases (e.g., low pressure gases or very small characteristic length scales in microchannels) the molecular collision frequency can be significantly reduced, limiting local thermodynamic equilibrium. In such cases, the continuum equations may remain valid as long as appropriate boundary conditions are used. As first explored by Maxwell in the late 1800s, it is important to understand the momentum and energy *accommodation* at gas-surface interfaces. The fluid interaction at solid surfaces depends on the surface roughness at the molecular scale. A perfectly mirror-surface (very rarely found in actual materials) reflects molecular collisions specularly. Because of molecular-scale roughness, the molecular collisions at actual surfaces reflect mostly diffusively (i.e., without any preferred direction). A tangential momentum accommodation coefficient can be defined as

\[ \sigma = \frac{\tau_i - \tau_r}{\tau_i - \tau_w}, \]  

(1.6)

where \( \tau_i \) is the incident momentum from the gas flow at a wall, \( \tau_r \) is the reflected momentum from the wall, and \( \tau_w \) is the wall momentum. If the wall is stationary then \( \tau_w = 0 \). If the reflection is perfectly diffusive (i.e., equal in all directions) then \( \tau_r = 0 \). The value of the accommodation coefficient is bounded as \( 0 \leq \sigma \leq 1 \), with \( \sigma \approx 1 \) for most practical surfaces. Maxwell proposed a first-order relationship for the slip velocity as

\[ u_s - u_w = \frac{2 - \sigma}{\sigma} L \left( \frac{\partial u}{\partial n} \right)_w, \]  

(1.7)

where \( u_s \) is the tangential velocity within one mean-free path length from the surface and \( u_w \) is the actual wall velocity (typically \( u_w = 0 \)). The derivative represents the gradient of the tangential velocity normal to the solid wall. Considering the gas flow in a small-diameter microchannel where the channel diameter is comparable to the mean-free path length, the *slip* boundary condition for a continuum fluid-mechanics model may be represented as

\[ u_w = \frac{2 - \sigma}{\sigma} L \left( \frac{\partial u}{\partial n} \right)_w. \]  

(1.8)
As the Knudsen number decreases (shorter mean-free path length), Eq. 1.7 tends toward the ordinary no-slip condition (i.e., for a stationary surface $u_w = 0$).

Equation 1.7 is the most straightforward slip boundary condition; it can be improved with higher-order representations. There are also analogous relationships for the temperature accommodation at a wall. That is, in high Knudsen number flows, the gas temperature at a solid surface may be different from the solid temperature. The present book is concerned primarily with continuum fluid mechanics, not rarefied gas dynamics where the fluid mean-free path lengths are comparable with characteristic reactor dimensions. However, even for relatively high Knudsen number flows, the continuum equations remain valid as long as boundary conditions accommodate the possibility of non-accommodation (i.e., slip).

### 1.4 Chemically Reacting Fluid Flow

Some of the most complex chemically reacting flow problems involve combustion. Fully modeling most practical combustion devices, such as automobile engines, gas-turbine combustors, or industrial furnaces, requires a three-dimensional geometrical representation, turbulence models, and models for the chemistry of complex fuels (e.g., jet fuel). Even with modern parallel supercomputers, such problems are usually much too complex to be solved with elementary chemical kinetics (i.e., thousands of reactions) and a full fluid-mechanical description. Therefore, in practical terms, some simplification is necessary. One option is to concentrate on modeling the details of combustion chemistry and flame structure in idealized laboratory settings. Such modeling efforts are used to establish a fundamental understanding of flame structure and to provide insight about the behavior of practical systems. In cases where fluid mechanical and geometric complexities are needed, the chemistry must usually be represented in terms of “reduced” reaction mechanisms or relatively simpler “global” reactions.

There has been a great deal of research on the combustion of small hydrocarbons, including nitrogen-cycle chemistry leading to nitric-oxide formation and abatement [2]. A number of methane-air reaction mechanisms have been developed and validated [3–5], with
the most popular one being GRI-Mech [6]. There is also a great deal of active research on
the kinetics of large-hydrocarbon combustion, such as for jet fuels.

Perhaps the most studied laboratory flame is the laminar premixed flat flame. As illustrated in the left-hand panel of Fig. 1.2, a steady flame is established above a porous burner face. Such flames are used widely in combustion laboratories, where a variety of optical and probe-based diagnostics are used to measure species and temperature profiles. Models play an essential role in assisting the interpretation of the data. In addition to the premixed flat flame, there are a great many other laboratory flames, including opposed-flow and co-flow geometries.

Materials processing, via approaches such as CVD, is an important application of chemically reacting flow. These processes are used widely, for example, in the production of silicon-based semiconductors, compound semiconductors, optoelectronics, photovoltaics, or other thin-film electronic materials. Quite often, materials processing is done in reactors with reactive gases at less than atmospheric pressure. In this case, owing to the fact that reducing pressure increases diffusive transport compared to inertial transport, the flows tend to remain laminar.

The present text is concerned exclusively with laminar flows; turbulence is not discussed. However, the complexities of multicomponent molecular transport of mass, momentum, and energy are discussed, especially for gas mixtures. Kinetic-theory formalisms are used to determine mixture viscosity and thermal conductivity, as well as multicomponent ordinary and thermal diffusion coefficients. It should at least be noted that a variety of laminar strained flames have been developed and studied specifically because of the insight they offer for understanding turbulent flame environments.

Generally speaking, the present book concentrates on low-speed, “weakly compressible,” gas flows, which in some respects behave as incompressible flows. In typical situations, such as a flame, there are large temperature variations in the flow field, and hence large density variations. Even with the large density variations, the flows are gas-dynamically incompressible in the sense that low-amplitude pressure waves (sound) have a negligible effect on the flow field. As a result the pressure field can be “filtered,” leaving a spatially uniform thermodynamic pressure that is used in property evaluation. The Navier–Stokes equations must retain the pressure gradients, which have a large influence on the flow. However, the energy transport can generally neglect any effects associated with pressure field.

This book is concerned with both homogeneous gas-phase chemistry and heterogeneous surface chemistry. Certainly in combustion, gas-phase chemistry is usually dominant. However, there may also be good reason to be concerned with heterogeneous chemistry, such as on the relatively cool walls of a combustion chamber. Moreover, there are emerging materials-synthesis and surface-modification techniques that depend on gas-surface interactions.

1.5 Physical Chemistry

Chemical kinetics and thermochemistry are important components in reacting flow simulations. Even modestly sized reaction mechanisms for combustion systems typically involve
scores of chemical species and hundreds of reactions. The reaction rates (kinetics) govern how fast the combustion proceeds, while the thermochemistry governs heat release and equilibrium behavior. In many cases the analyst can use a reaction mechanism that has been developed and tested by others. In other situations a particular chemical system may not have been previously studied, and through coordinated experiments and simulation the goal is to determine the key reaction pathways and associated rate expressions. Successfully modeling reactive flows requires some familiarity with aspects of physical chemistry to understand the inputs to the simulation and to interpret the predicted results.

This book is surely not intended to cover all aspects of physical chemistry. However, there is an attempt to provide sufficient theoretical background for the reader with training in mechanical or chemical engineering to understand what is needed to develop and analyze chemically reacting flow models. This includes understanding the chemistry input parameters that someone else has determined and, more important, being able to estimate parameters that are needed to do a simulation but simply do not exist in the literature.

Statistical thermodynamics is discussed as a means of understanding and estimating thermochemical properties of chemical species. This treatment also lays the groundwork for a subsequent discussion of reaction rate theories. Mass-action kinetics are usually assumed to govern the rates of chemical reactions. A general framework for chemical rate expressions suitable for accommodating large reaction mechanisms is presented. However, often the rate of an individual chemical reaction is unknown, and must be estimated in some manner. The chapter on Reaction Rate Theories discusses a number of theoretical treatments, with differing degrees of rigor, that are used to understand and estimate individual chemical reaction rates. An accompanying chapter treats chemical reactions occurring at a gas-surface interface, important for applications such as catalysis and materials processing. Many aspects of molecular transport are also discussed, from estimating transport properties of individual species to the driving forces and governing equations for gas-phase mass transport.

1.6 Illustrative Examples

The theoretical approaches developed in this book are quite general, enabling treatment of a wide variety of flow situations and process chemistries. The intent of this section, which briefly discusses a few recent applications, is to present representative illustrations of types of problems that the book considers.

As mentioned in Section 1.4, laminar premixed flat flames are used widely in the study of combustion chemistry. The left-hand panel of Fig. 1.2 shows a typical burner setup. The flames themselves are accessible to an array of physical and optical diagnostics, and the computational models can incorporate the details of elementary chemical reactions. Often the flames are operated at sub-atmospheric pressure to enhance molecular diffusive processes, leading to thicker flames that are more easily probed.

The right-hand panel of Fig. 1.2 illustrates an opposed-flow diffusion-flame arrangement. Here the fuel and oxidizer flows are separated, only coming together at the flame. Both premixed and non-premixed flames find use in practical combustion devices. Thus, it is important to model and understand the behaviors of both types of flames, as well as
ILLUSTRATIVE EXAMPLES

1.3

Illustration of a stagnation-flame configuration for the deposition of a polycrystalline diamond film. The photograph of the flame itself shows a highly luminous flat flame just above the deposition surface.

Figure 1.3 Illustration of a stagnation-flame configuration for the deposition of a polycrystalline diamond film. The photograph of the flame itself shows a highly luminous flat flame just above the deposition surface.

The opposed contraction nozzles illustrated in Fig. 1.2 produces a highly desirable flow similarity that facilitates modeling and data interpretation.

Flat flames can be made to impinge onto surfaces. Such “strained” flames can be used for a variety of purposes. On the one hand, these flames can be used in the laboratory to study the effects of strain on flame structure, and thus improve understanding of the fluid-mechanical effects encountered in turbulent flows. It may also be interesting to discover how a cool surface (e.g., an engine or furnace wall) affects flame structure. Even though the stagnation-flow situation is two-dimensional in the sense that there are two velocity components, the problem can be reduced to a one-dimensional model by “similarity,” as derived and discussed in Chapter 7.

Some interesting materials-processing applications take advantage of flames that impinge on surfaces. Figure 1.3 illustrates an atmospheric-pressure premixed flow of acetylene, hydrogen, and oxygen issues from a flat burner face onto a hot parallel flat surface. The purpose of this configuration is to grow polycrystalline diamond films [7, 8]. Models of such processes must consider the details of both homogeneous and heterogeneous chemical kinetics, coupled with the fluid flow [9]. Other flame-diamond processes use a similar flow configuration, but with low-pressure, burner-stabilized flames [10]. In addition to CVD processes to deposit films, flames can be used to “modify” surfaces. For example, the high free-radical concentrations in flames are used to alter the structure of polymer films [11] or metals [12].

Mathematically, there is very little difference between the configuration shown in Fig. 1.3 and the one in which two flat “burners” face each other in an opposed-flow configuration (Fig. 1.2). There are many commonly used variants of the opposed-flow geometry. For example, premixed combustible gases could issue from both burner faces, causing twin...
premixed flames. Alternatively, fuel could issue from one side and oxidizer from the other, causing a non-premixed flame (diffusion flame).

Stagnation flow is used as the basis of many CVD processes. A typical configuration, as illustrated in Fig. 1.4, consists of a flat “showerhead” manifold and a parallel, flat deposition surface. The inlet manifold and deposition susceptor, on which a wafer is held, are controlled to maintain a fixed temperature. The simulation shown on the right-hand side of Fig. 1.4 comes from a two-dimensional axisymmetric flow model that represents actual reactor geometry. In this reactor the chemically active precursors enter through a showerhead manifold and an inert purge gas flows in the annular space near the walls. The stagnation surface is maintained at high temperature, and the walls and the inlet gases are relatively cool. The gray scales indicate the concentration of yttrium-tetramethyl-heptanediionate, which is one of the metal-organic precursor gases. Notice that the species profiles in the gas phase above the deposition surface are essentially flat, that is, they have little radial variation. This is exactly the behavior that is required to realize the stagnation-flow similarity on which the one-dimensional models are based.

Figure 1.5 Illustration of the chemically reacting boundary-layer flow in a single channel of a catalytic-combustion monolith.
The chemically reacting flow in channels and ducts, which may or may not have surface chemistry on the walls, is a commonly encountered situation. The example illustrated in Fig. 1.5 considers the oxidation of a lean premixed methane-air flow in the channel of a catalytic-combustion monolith with platinum-coated walls [13]. Depending on the channel size, flow rates, and chemistry details, different levels of conservation-equation reduction may be appropriate. At the simplest level there are situations in which a plug-flow representation may be adequate. Plug flow presumes that there are no radial variations across the channel and that axial diffusive transport is negligible. Even considering elementary surface chemistry, the plug-flow model is formulated as a set of ordinary differential equations, with the axial coordinate being the independent variable.

From the solution shown in Fig. 1.5, it is evident that a plug-flow representation is not appropriate. That is to say, the species profiles clearly have radial dependence. However, for these flow conditions (which are typical), a boundary-layer approximation is appropriate. In fact, based on direct comparison between full Navier–Stokes models and boundary-layer models, it can be shown that the boundary-layer models are accurate [13]. Moreover, the boundary-layer models are very much faster to solve compared to the Navier–Stokes models, especially when complex gas-phase chemistry is involved.

Figure 1.6 illustrates a channel-flow reactor that can be used for a variety of semiconductor-processing applications. A combustion-based process is being used to oxidize silicon surfaces, leading to high-quality gate oxides in semiconductor devices [14]. In this process a mixture of hydrogen and oxygen flows over a silicon wafer that is heated to around 1000°C. A series of gas-phase reactions leads to the production of atomic oxygen, which is a highly effective oxidizing agent [15]. This process has been modeled using both stirred-reactor and boundary-layer models [15].

Figure 1.7 illustrates a counter-flow microchannel reactor. Alternating layers house catalysts that are designed to accomplish specific chemical processes [16, 17]. The reactor illustrated here is configured as a methane-steam reformer whose objective is to accomplish a global reaction as \( \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO} \). This is a highly endothermic reaction, requiring significant heat input to maintain reaction temperatures around 700 °C. The non-catalytic channel layers are used to house a high-temperature fluid that transfers heat to the
catalytic channels [18, 19]. In this technology the individual channels have characteristic hydraulic diameters on the order of a millimeter, with the fluids remaining laminar within the channels. Despite the laminar flow (as compared to turbulent flow), the small characteristic dimensions lead to very high heat and mass transfer rates. These high rates, in turn, lead to high performance in compact reactors. Such microchannel technology is also widely used in high-performance heat exchangers [20, 21].

Figure 1.8 illustrates a planar solid-oxide fuel cell (SOFC), which is a technology that is capable of converting hydrocarbon fuels to electricity [22–26]. In such a fuel-cell architecture the flow channels have small characteristic dimensions, typically on the order of a millimeter. Oxygen ions are conducted through a thin electrolyte membrane, whereupon they react with the fuel flow. This electrochemical “combustion” reaction (i.e., fuel oxidation) involves gas-phase transport and chemistry, as well as heterogeneous catalysis and electrochemistry. Critical aspects of fuel-cell design and optimization require understanding the complexities of chemically reacting flow, with modeling offering important contributions. For direct oxidation of hydrocarbon fuels (e.g., natural gas), the possibility of forming aromatic compounds and carbon deposits is an important system consideration, which depends critically on the chemical kinetics and the chemically reacting flow. Depending on flow rates and channel dimensions, boundary-layer or plug-flow models may be appropriate. In either case a predictive chemical reaction mechanism must be able to represent fuel pyrolysis and oxidation, including the formation of higher hydrocarbons.

In addition to chemically reacting flow within small channels (e.g., Fig. 1.8), fuel-cell and related technologies depend on chemically reacting flow and transport within porous media as well as electrochemical reactions at electrode–electrolyte interfaces. Figure 1.9 illustrates a laboratory-scale fuel-cell membrane-electrode assembly, focusing on transport and chemistry within the porous composite anode structure. The fuel and oxidizer (e.g., air) are separated by a membrane-electrode assembly, comprised of an anode (negative electrode), electrolyte membrane, and cathode (positive electrode). In solid oxide fuel cell
Figure 1.8  Segment of a planar, anode-supported, solid-oxide fuel cell (SOFC), where a membrane-electrode assembly (MEA) is sandwiched between an interconnect structure that forms fuel and air channels. With hydrocarbon fuels, catalytic reforming chemistry is promoted within the ceramic-metallic composite anode structure. There may also be homogeneous chemical reaction within the flow channels. Electrochemical charge-transfer reactions proceed at the interfaces between electrode and electrolyte materials. A counter-flow situation is illustrated here, but co-flow and cross-flow configurations are also common. Channel cross section dimensions are typically on the order of a millimeter. Source: Kee, et al. [22]. Reproduced with permission of Elsevier.

(SOFC) technology the electrolyte membrane is an oxygen-ion conductor. The role of the cathode is to electro-catalytically reduce air to oxygen ions (e.g., \( O_2 + e^- \rightleftharpoons 2O^{2-} \)), which are mobile within the electrolyte membrane. The role of the anode is to electro-catalytically oxidize the fuel (e.g., \( H_2 + O^{2-} \rightleftharpoons H_2O + 2e^- \)), producing electrons that enter an external circuit (i.e., an electrical load).

As illustrated by the expanded view in Fig. 1.9, the composite anode is a multifunctional porous ceramic-metallic composite. The metallic phase (e.g., nickel) is an electron conductor and the ceramic phase (e.g., yttria-stabilized zirconia) is an oxygen-ion conductor. Reactive gases (fuel and products) are mobile within the open porous structure. In addition to being the electronic conductor, the Ni surfaces also serve as a reforming catalyst when hydrocarbon fuels are involved. The electrochemical charge-transfer reactions take place at the so-called three-phase boundaries (TPB) at the intersections between the electrode, electrolyte, and gas phases. Chapters 17 and 18 focus on the theory and modeling approaches for predicting chemically reacting porous-media transport and electrochemical charge transfer.

Figure 1.10 illustrates some of the salient features within an interdigitated redox flow battery layout [27]. Small rectangular flow channels are situated within the bipolar plates. The “feed” channels are completely closed at the exit end of the structure, and “exhaust” channels are completely closed at the entrance end of the structure. Thus, all the fluid (electrolyte) that enters the feed channels must flow through the porous electrodes and leave
via the exhaust channels. Electrochemical reactions proceed within the porous electrodes, with ion mobility across the membrane that separates the anode and cathode.

Flow within the channels can be modeled with plug-flow assumptions (Chapter 5), predicting the local velocities and pressures. The feed and exhaust channels are coupled via the flow through the adjacent porous electrode structures (Chapter 17). The charge-transfer electrochemistry within the porous electrodes and the ion transport through membrane that
Figure 1.11 Catalytic annular membrane reactors, one for steam reforming and the other for partial oxidation.

separates the anode and cathode can be modeled using the concepts introduced in Chapter 18.

Figure 1.11 shows two catalytic membrane reactors, one with a hydrogen-permeable membrane and the other with an oxygen-permeable membrane. Both have packed-bed catalysts housed within the interior tube (Chapters 16 and 17). The steam-reforming reactor can be equilibrium limited. That is, once a certain concentration of the product $\text{H}_2$ is achieved, the reaction equilibrates and no further $\text{CH}_4$ conversion is possible. However, if $\text{H}_2$ is removed via a membrane, the equilibrium is shifted and further methane conversion can proceed. In the partial-oxidation reactor, there are thermal-control advantages to adding the oxygen along the length of the reactor rather than premixing the oxygen with the fuel. Depending on the membrane technology, there are also potential advantages to using the membrane for the in situ separation of oxygen from air.

REFERENCES


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INTRODUCTION


