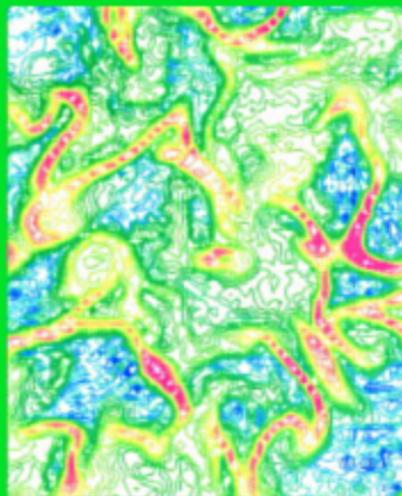


Computational Models for Turbulent Reacting Flows



Rodney O. Fox

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Computational Models for Turbulent Reacting Flows

This book presents the current state of the art in computational models for turbulent reacting flows, and analyzes carefully the strengths and weaknesses of the various techniques described. The focus is on formulation of practical models as opposed to numerical issues arising from their solution.

A theoretical framework based on the one-point, one-time joint probability density function (PDF) is developed. It is shown that all commonly employed models for turbulent reacting flows can be formulated in terms of the joint PDF of the chemical species and enthalpy. Models based on direct closures for the chemical source term as well as transported PDF methods, are covered in detail. An introduction to the theory of turbulence and turbulent scalar transport is provided for completeness.

The book is aimed at chemical, mechanical, and aerospace engineers in academia and industry, as well as developers of computational fluid dynamics codes for reacting flows.

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Computational Models for Turbulent Reacting Flows

Rodney O. Fox

*Herbert L. Stiles Professor of Chemical Engineering
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à Roberte

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Preface

In setting out to write this book, my main objective was to provide a reasonably complete introduction to computational models for turbulent reacting flows for students, researchers, and industrial end-users new to the field. The focus of the book is thus on the *formulation* of models as opposed to the numerical issues arising from their solution. Models for turbulent reacting flows are now widely used in the context of computational fluid dynamics (CFD) for simulating chemical transport processes in many industries. However, although CFD codes for non-reacting flows and for flows where the chemistry is relatively insensitive to the fluid dynamics are now widely available, their extension to reacting flows is less well developed (at least in commercial CFD codes), and certainly less well understood by potential end-users. There is thus a need for an introductory text that covers all of the most widely used reacting flow models, and which attempts to compare their relative advantages and disadvantages for particular applications.

The primary intended audience of this book comprises graduate-level engineering students and CFD practitioners in industry. It is assumed that the reader is familiar with basic concepts from chemical-reaction-engineering (CRE) and transport phenomena. Some previous exposure to theory of turbulent flows would also be very helpful, but is not absolutely required to understand the concepts presented. Nevertheless, readers who are unfamiliar with turbulent flows are encouraged to review Part I of the recent text *Turbulent Flows* by Pope (2000) before attempting to tackle the material in this book. In order to facilitate this effort, I have used the same notation as Pope (2000) whenever possible. The principal differences in notation occur in the treatment of multiple reacting scalars. In general, vector/matrix notation is used to denote the collection of thermodynamic variables (e.g., concentrations, temperature) needed to describe a reacting flow. Some familiarity with basic linear algebra and elementary matrix operations is assumed.

The choice of models to include in this book was dictated mainly by their ability to treat the wide range of turbulent reacting flows that occur in technological applications of interest to chemical engineers. In particular, models that cannot treat ‘general’ chemical

kinetics have been excluded. For example, I do not discuss models developed for premixed turbulent combustion based on the ‘turbulent burning velocity’ or on the ‘level-set’ approach. This choice stems from my desire to extend the CRE approach for modeling reacting flows to be compatible with CFD codes. In this approach, the exact treatment of the chemical kinetics is the *sine qua non* of a good model. Thus, although most of the models discussed in this work can be used to treat non-premixed turbulent combustion, this will not be our primary focus. Indeed, in order to keep the formulation as simple as possible, all models are presented in the context of constant-density flows. In most cases, the extension to variable-density flows is straightforward, and can be easily undertaken after the reader has mastered the application of a particular model to constant-density cases.

In order to compare various reacting-flow models, it is necessary to present them all in the same conceptual framework. In this book, a statistical approach based on the one-point, one-time joint probability density function (PDF) has been chosen as the common theoretical framework. A similar approach can be taken to describe turbulent flows (Pope 2000). This choice was made due to the fact that nearly all CFD models currently in use for turbulent reacting flows can be expressed in terms of quantities derived from a joint PDF (e.g., low-order moments, conditional moments, conditional PDF, etc.). Ample introductory material on PDF methods is provided for readers unfamiliar with the subject area. Additional discussion on the application of PDF methods in turbulence can be found in Pope (2000). Some previous exposure to engineering statistics or elementary probability theory should suffice for understanding most of the material presented in this book.

The material presented in this book is divided into seven chapters and two appendices. Chapter 1 provides background information on turbulent reacting flows and on the two classical modeling approaches (chemical-reaction-engineering and fluid-mechanical) used to describe them. The chapter ends by pointing out the similarity between the two approaches when dealing with the effect of molecular mixing on chemical reactions, especially when formulated in a Lagrangian framework.

Chapter 2 reviews the statistical theory of turbulent flows. The emphasis, however, is on collecting in one place all of the necessary concepts and formulae needed in subsequent chapters. The discussion of these concepts is necessarily brief, and the reader is referred to Pope (2000) for further details. It is, nonetheless, essential that the reader become familiar with the basic scaling arguments and length/time scales needed to describe high-Reynolds-number turbulent flows. Likewise, the transport equations for important one-point statistics in inhomogeneous turbulent flows are derived in Chapter 2 for future reference.

Chapter 3 reviews the statistical description of scalar mixing in turbulent flows. The emphasis is again on collecting together the relevant length and time scales needed to describe turbulent transport at high Reynolds/Schmidt numbers. Following Pope (2000), a model scalar energy spectrum is constructed for stationary, isotropic scalar fields. Finally, the transport equations for important one-point scalar statistics in inhomogeneous turbulent mixing are derived in Chapter 3.

In order to model turbulent reacting flows accurately, an accurate model for turbulent transport is required. In Chapter 4 I provide a short introduction to selected computational models for *non-reacting* turbulent flows. Here again, the goal is to familiarize the reader with the various options, and to collect the most important models in one place for future reference. For an in-depth discussion of the physical basis of the models, the reader is referred to Pope (2000). Likewise, practical advice on choosing a particular turbulence model can be found in Wilcox (1993).

With regards to reacting flows, the essential material is presented in Chapters 5 and 6. Chapter 5 focuses on reacting flow models that can be expressed in terms of Eulerian (as opposed to Lagrangian) transport equations. Such equations can be solved numerically using standard finite-volume techniques, and thus can be easily added to existing CFD codes for turbulent flows. Chapter 6, on the other hand, focuses on *transported PDF* or *full PDF* methods. These methods typically employ a Lagrangian modeling perspective and ‘non-traditional’ CFD methods (i.e., Monte-Carlo simulations). Because most readers will not be familiar with the numerical methods needed to solve transported PDF models, an introduction to the subject is provided in Chapter 7.

Chapter 5 begins with an overview of chemical kinetics and the chemical-source-term closure problem in turbulent reacting flows. Based on my experience, closure methods based on the moments of the scalars are of very limited applicability. Thus, the emphasis in Chapter 5 is on presumed PDF methods and related closures based on conditioning on the mixture fraction. The latter is a non-reacting scalar that describes mixing between non-premixed inlet streams. A general definition of the mixture-fraction vector is derived in Chapter 5. Likewise, it is shown that by using a so-called ‘mixture-fraction’ transformation it is possible to describe a turbulent reacting flow by a reduced set of scalars involving the mixture-fraction vector and a ‘reaction-progress’ vector. Assuming that the mixture-fraction PDF is known, we introduce closures for the reaction-progress vector based on chemical equilibrium, ‘simple’ chemistry, laminar diffusion flamelets, and conditional moment closures. Closures based on presuming a form for the PDF of the reacting scalars are also considered in Chapter 5.

Chapter 6 presents a relatively complete introduction to transported PDF methods for turbulent reacting flow. For these flows, the principal attraction of transported PDF methods is the fact that the highly non-linear chemical source term is treated without closure. Instead, the modeling challenges are shifted to the molecular mixing model, which describes the combined effects of turbulent mixing (i.e., the scalar length-scale distribution) and molecular diffusion on the joint scalar PDF. Because the transported PDF treatment of turbulence is extensively discussed in Pope (2000), I focus in Chapter 6 on modeling issues associated with molecular mixing. The remaining sections in Chapter 6 deal with Lagrangian PDF methods, issues related to estimation of statistics based on ‘particle’ samples, and with tabulation methods for efficiently evaluating the chemical source term.

Chapter 7 deviates from the rest of the book in that it describes computational *methods* for ‘solving’ the transported PDF transport equation. Although Lagrangian PDF codes are

generally preferable to Eulerian PDF codes, I introduce both methods and describe their relative advantages and disadvantages. Because transported PDF codes are less developed than standard CFD methods, readers wishing to utilize these methods should consult the literature for recent advances.

The material covered in the appendices is provided as a supplement for readers interested in more detail than could be provided in the main text. Appendix A discusses the derivation of the spectral relaxation (SR) model starting from the scalar spectral transport equation. The SR model is introduced in Chapter 4 as a non-equilibrium model for the scalar dissipation rate. The material in Appendix A is an attempt to connect the model to a more fundamental description based on two-point spectral transport. This connection can be exploited to extract model parameters from direct-numerical simulation data of homogeneous turbulent scalar mixing (Fox and Yeung 1999).

Appendix B discusses a new method (DQMOM) for solving the Eulerian transported PDF transport equation without resorting to Monte-Carlo simulations. This offers the advantage of solving for the joint composition PDF introduced in Chapter 6 using standard finite-volume CFD codes, without resorting to the chemical-source-term closures presented in Chapter 5. Preliminary results found using DQMOM are quite encouraging, but further research will be needed to understand fully the range of applicability of the method.

I am extremely grateful to the many teachers, colleagues and graduate students who have helped me understand and develop the material presented in this work. In particular, I would like to thank Prof. John C. Matthews of Kansas State University who, through his rigorous teaching style, attention to detail, and passion for the subject of transport phenomena, first planted the seed in the author that has subsequently grown into the book that you have before you. I would also like to thank my own students in the graduate courses that I have offered on this subject who have provided valuable feedback about the text. I want especially to thank Kuochen Tsai and P. K. Yeung, with whom I have enjoyed close collaborations over the past several years, and Jim Hill at Iowa State for his encouragement to undertake the writing of this book. I would also like to acknowledge the important contributions of Daniele Marchisio in the development of the DQMOM method described in Appendix B.

For his early support and encouragement to develop CFD models for chemical-reaction-engineering applications, I am deeply indebted to my post-doctoral advisor, Jacques Villiermaux. His untimely death in 1997 was a great loss to his friends and family, as well as to the profession.

I am also deeply indebted to Stephen Pope in many different ways, starting from his early encouragement in 1991 to consider PDF methods as a natural modeling framework for describing micromixing in chemical reactors. However, I am particularly grateful that his text on turbulent flows appeared before this work (relieving me of the arduous task of covering this subject in detail!), and for his generosity in sharing early versions of his text, as well as his \LaTeX macro files and precious advice on preparing the manuscript.

Beginning with a Graduate Fellowship, my research in turbulent reacting flows has been almost continuously funded by research grants from the US National Science Foundation. This long-term support has made it possible for me to pursue novel research ideas outside the traditional modeling approach used by chemical reaction engineers. In hindsight, the application of CFD to chemical reactor design and analysis appears to be a rather natural idea. Indeed, all major chemical producers now use CFD tools routinely to solve day-to-day engineering problems. However, as recently as the 1990s the gap between chemical reaction engineering and fluid mechanics was large, and only through a sustained effort to understand both fields in great detail was it possible to bridge this gap. While much research remains to be done to develop a complete set of CFD tools for chemical reaction engineering (most notably in the area of *multiphase* turbulent reacting flows), one is certainly justified in pointing to computational models for turbulent reacting flows as a highly successful example of fundamental academic research that has led to technological advances in real-world applications. Financial assistance provided by my industrial collaborators: Air Products, BASF, BASELL, Dow Chemical, DuPont, and Fluent, is deeply appreciated.

I also want to apologize to my colleagues in advance for not mentioning many of their excellent contributions to the field of turbulent reacting flows that have appeared over the last 50 years. It was my original intention to include a section in Chapter 1 on the history of turbulent-reacting-flow research. However, after collecting the enormous number of articles that have appeared in the literature to date, I soon realized that the task would require more time and space than I had at my disposal in order to do it justice. Nonetheless, thanks to the efforts of Jim Herriott at Iowa State, I have managed to include an extensive Reference section that will hopefully serve as a useful starting point for readers wishing to delve into the history of particular subjects in greater detail.

Finally, I dedicate this book to my wife, Roberte. Her encouragement and constant support during the long period of this project and over the years have been invaluable.

Turbulent reacting flows

1.1 Introduction

At first glance, to the uninitiated the subject of turbulent reacting flows would appear to be relatively simple. Indeed, the basic governing principles can be reduced to a statement of conservation of chemical species and energy ((1.28), p. 16) and a statement of conservation of fluid momentum ((1.27), p. 16). However, anyone who has attempted to master this subject will tell you that it is in fact quite complicated. On the one hand, in order to understand how the fluid flow affects the chemistry, one must have an excellent understanding of turbulent flows and of turbulent mixing. On the other hand, given its paramount importance in the determination of the types and quantities of chemical species formed, an equally good understanding of chemistry is required. Even a cursory review of the literature in any of these areas will quickly reveal the complexity of the task. Indeed, given the enormous research production in these areas during the twentieth century, it would be safe to conclude that no one could simultaneously master all aspects of turbulence, mixing, and chemistry.

Notwithstanding the intellectual challenges posed by the subject, the main impetus behind the development of computational models for turbulent reacting flows has been the increasing awareness of the impact of such flows on the environment. For example, incomplete combustion of hydrocarbons in internal combustion engines is a major source of air pollution. Likewise, in the chemical process and pharmaceutical industries, inadequate control of product yields and selectivities can produce a host of undesirable byproducts. Even if such byproducts could all be successfully separated out and treated so that they are not released into the environment, the economic cost of doing so is often prohibitive. Hence, there is an ever-increasing incentive to improve industrial processes and devices in order for them to remain competitive in the marketplace.

Given their complexity and practical importance, it should be no surprise that different approaches for dealing with turbulent reacting flows have developed over the last 50 years. On the one hand, the chemical-reaction-engineering (CRE) approach came from the application of chemical kinetics to the study of chemical reactor design. In this approach, the details of the fluid flow are of interest only in as much as they affect the product yield and selectivity of the reactor. In many cases, this effect is of secondary importance, and thus in the CRE approach greater attention has been paid to other factors that directly affect the chemistry. On the other hand, the fluid-mechanical (FM) approach developed as a natural extension of the statistical description of turbulent flows. In this approach, the emphasis has been primarily on how the fluid flow affects the rate of chemical reactions. In particular, this approach has been widely employed in the study of combustion (Rosner 1986; Peters 2000; Poinso and Veynante 2001; Veynante and Vervisch 2002).

In hindsight, the primary factor in determining which approach is most applicable to a particular reacting flow is the characteristic time scales of the chemical reactions relative to the turbulence time scales. In the early applications of the CRE approach, the chemical time scales were larger than the turbulence time scales. In this case, one can safely ignore the details of the flow. Likewise, in early applications of the FM approach to combustion, all chemical time scales were assumed to be much smaller than the turbulence time scales. In this case, the details of the chemical kinetics are of no importance, and one is free to concentrate on how the heat released by the reactions interacts with the turbulent flow. More recently, the shortcomings of each of these approaches have become apparent when applied to systems wherein some of the chemical time scales overlap with the turbulence time scales. In this case, an accurate description of both the turbulent flow and the chemistry is required to predict product yields and selectivities accurately.

With these observations in mind, the reader may rightly ask ‘What is the approach used in this book?’ The accurate answer to this question may be ‘both’ or ‘neither,’ depending on your perspective. From a CRE perspective, the methods discussed in this book may appear to favor the FM approach. Nevertheless, many of the models find their roots in CRE, and one can argue that they have simply been rewritten in terms of detailed transport models that can be solved using computational fluid dynamics (CFD) techniques (Fox 1996a; Harris *et al.* 1996; Ranada 2002). Likewise, from an FM perspective, very little is said about the details of turbulent flows or the computational methods needed to study them. Instead, we focus on the models needed to describe the source term for chemical reactions involving *non-premixed* reactants. Moreover, for the most part, density variations in the fluid due to mixing and/or heat release are not discussed in any detail. Otherwise, the only criterion for including a particular model in this book is the requirement that it must be able to handle detailed chemistry. This criterion is motivated by the need to predict product yield and selectivity accurately for finite-rate reactions.

At first glance, the exclusion of premixed reactants and density variations might seem to be too drastic. (Especially if one equates ‘turbulent reacting flows’ with ‘combustion.’¹)

¹ Excellent treatments of modern approaches to combustion modeling are available elsewhere (Kuznetsov and Sabel'nikov 1990; Warnatz *et al.* 1996; Peters 2000; Poinso and Veynante 2001).

However, if one looks at the complete range of systems wherein turbulence and chemistry interact, one will find that many of the so-called ‘mixing-sensitive’ systems involve liquids or gas-phase reactions with modest density changes. For these systems, a key feature that distinguishes them from classical combusting systems is that the reaction rates are fast regardless of the temperature (e.g., acid–base chemistry). In contrast, much of the dynamical behavior of typical combusting systems is controlled by the fact that the reactants do not react at ambient temperatures. Combustion can thus be carried out in either premixed or non-premixed modes, while mixing-sensitive reactions can only be carried out in non-premixed mode. This distinction is of considerable consequence in the case of premixed combustion. Indeed, models for premixed combustion occupy a large place unto themselves in the combustion literature. On the other hand, the methods described in this book will find utility in the description of non-premixed combustion. In fact, many of them originated in this field and have already proven to be quite powerful for the modeling of diffusion flames with detailed chemistry.

In the remainder of this chapter, an overview of the CRE and FM approaches to turbulent reacting flows is provided. Because the description of turbulent flows and turbulent mixing makes liberal use of ideas from probability and statistical theory, the reader may wish to review the appropriate appendices in Pope (2000) before starting on Chapter 2. Further guidance on how to navigate the material in Chapters 2–7 is provided in Section 1.5.

1.2 Chemical-reaction-engineering approach

The CRE approach for modeling chemical reactors is based on mole and energy balances, chemical rate laws, and idealized flow models.² The latter are usually constructed (Wen and Fan 1975) using some combination of plug-flow reactors (PFRs) and continuous-stirred-tank reactors (CSTRs). (We review both types of reactors below.) The CRE approach thus avoids solving a detailed flow model based on the momentum balance equation. However, this simplification comes at the cost of introducing unknown model parameters to describe the flow rates between various sub-regions inside the reactor. The choice of a particular model is far from unique,³ but can result in very different predictions for product yields with complex chemistry.

For isothermal, first-order chemical reactions, the mole balances form a system of *linear* equations. A non-ideal reactor can then be modeled as a collection of *Lagrangian* fluid elements moving *independently* through the system. When parameterized by the amount of time it has spent in the system (i.e., its residence time), each fluid element behaves as a batch reactor. The species concentrations for such a system can be completely characterized by the inlet concentrations, the chemical rate constants, and the residence time distribution (RTD) of the reactor. The latter can be found from simple tracer experiments carried out under identical flow conditions. A brief overview of RTD theory is given below.

² In CRE textbooks (Hill 1977; Levenspiel 1998; Fogler 1999), the types of reactors considered in this book are referred to as *non-ideal*. The flow models must take into account fluid-mixing effects on product yields.

³ It has been described as requiring ‘a certain amount of art’ (Fogler 1999).

For non-isothermal or non-linear chemical reactions, the RTD no longer suffices to predict the reactor outlet concentrations. From a Lagrangian perspective, local *interactions* between fluid elements become important, and thus fluid elements cannot be treated as individual batch reactors. However, an accurate description of fluid-element interactions is strongly dependent on the underlying fluid flow field. For certain types of reactors, one approach for overcoming the lack of a detailed model for the flow field is to input empirical flow correlations into so-called *zone* models. In these models, the reactor volume is decomposed into a finite collection of well mixed (i.e., CSTR) zones connected at their boundaries by molar fluxes.⁴ (An example of a zone model for a stirred-tank reactor is shown in Fig. 1.5.) Within each zone, all fluid elements are assumed to be identical (i.e., have the same species concentrations). Physically, this assumption corresponds to assuming that the chemical reactions are slower than the local *micromixing time*.⁵

For non-linear chemical reactions that are fast compared with the local micromixing time, the species concentrations in fluid elements located in the same zone cannot be assumed to be identical (Toor 1962; Toor 1969; Toor and Singh 1973; Amerja *et al.* 1976). The canonical example is a non-premixed acid–base reaction for which the reaction rate constant is essentially infinite. As a result of the infinitely fast reaction, a fluid element can contain either acid or base, but not both. Due to the chemical reaction, the local fluid-element concentrations will therefore be different depending on their stoichiometric excess of acid or base. Micromixing will then determine the rate at which acid and base are transferred between fluid elements, and thus will determine the mean rate of the chemical reaction.

If all chemical reactions are fast compared with the local micromixing time, a non-premixed system can often be successfully described in terms of the *mixture fraction*.⁶ The more general case of *finite-rate* reactions requires a detailed description of micromixing or, equivalently, the interactions between local fluid elements. In the CRE approach, micromixing is modeled using a Lagrangian description that follows individual fluid elements as they flow through the reactor. (Examples of micromixing models are discussed below.) A key parameter in such models is the micromixing time, which must be related to the underlying flow field.

For canonical turbulent flows (Pope 2000), the flow parameters required to complete the CRE models are readily available. However, for the complex flow fields present in most chemical reactors, the flow parameters must be found either empirically or by solving a CFD turbulence model. If the latter course is taken, the next logical step would be to attempt to reformulate the CRE model in terms of a set of transport equations that can be added to the CFD model. The principal complication encountered when following this path is the fact that the CRE models are expressed in a Lagrangian framework, whilst the CFD models are expressed in an *Eulerian* framework. One of the main goals of this book

⁴ The zones are thus essentially identical to the *finite volumes* employed in many CFD codes.

⁵ The micromixing time has an exact definition in terms of the rate of decay of *concentration fluctuations*.

⁶ The mixture fraction is defined in Chapter 5.

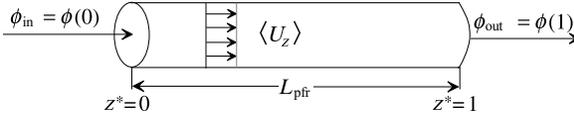


Figure 1.1. Sketch of a plug-flow reactor.

is thus to demonstrate how the two approaches can be successfully combined when both are formulated in terms of an appropriate statistical theory.

In the remainder of this section, we will review those components of the CRE approach that will be needed to understand the modeling approach described in detail in subsequent chapters. Further details on the CRE approach can be found in introductory textbooks on chemical reaction engineering (e.g., Hill 1977; Levenspiel 1998; Fogler 1999).

1.2.1 PFR and CSTR models

The PFR model is based on turbulent pipe flow in the limit where axial dispersion can be assumed to be negligible (see Fig. 1.1). The mean residence time τ_{pfr} in a PFR depends only on the mean axial fluid velocity $\langle U_z \rangle$ and the length of the reactor L_{pfr} :

$$\tau_{pfr} \equiv \frac{L_{pfr}}{\langle U_z \rangle}. \quad (1.1)$$

Defining the dimensionless axial position by $z^* \equiv z/L_{pfr}$, the PFR model for the species concentrations ϕ becomes⁷

$$\frac{d\phi}{dz^*} = \tau_{pfr} \mathbf{S}(\phi) \quad \text{with} \quad \phi(0) = \phi_{in} = \text{inlet concentrations}, \quad (1.2)$$

where \mathbf{S} is the *chemical source term*. Given the inlet concentrations and the chemical source term, the PFR model is readily solved using numerical methods for initial-value problems to find the outlet concentrations $\phi(1)$.

The PFR model ignores mixing between fluid elements at *different* axial locations. It can thus be rewritten in a Lagrangian framework by substituting $\alpha = \tau_{pfr} z^*$, where α denotes the elapsed time (or *age*) that the fluid element has spent in the reactor. At the end of the PFR, all fluid elements have the same age, i.e., $\alpha = \tau_{pfr}$. Moreover, at every point in the PFR, the species concentrations are uniquely determined by the age of the fluid particles at that point through the solution to (1.2).

In addition, the PFR model assumes that mixing between fluid elements at the *same* axial location is infinitely fast. In CRE parlance, all fluid elements are said to be *well micromixed*. In a tubular reactor, this assumption implies that the inlet concentrations are uniform over the cross-section of the reactor. However, in real reactors, the inlet streams are often segregated (non-premixed) at the inlet, and a finite time is required as they move down the reactor before they become well micromixed. The PFR model can be easily

⁷ The notation is chosen to be consistent with that used in the remainder of the book. Alternative notation is employed in most CRE textbooks.

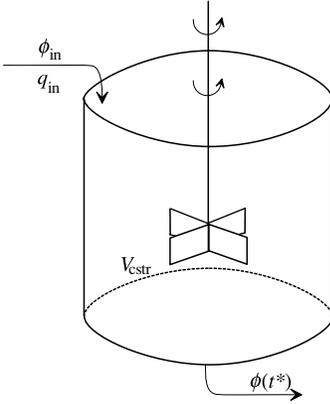


Figure 1.2. Sketch of a continuous-stirred-tank reactor (CSTR).

extended to describe radial mixing by introducing a micromixing model. We will look at a *poorly micromixed* PFR model below.

The CSTR model, on the other hand, is based on a stirred vessel with continuous inflow and outflow (see Fig. 1.2). The principal assumption made when deriving the model is that the vessel is stirred vigorously enough to eliminate all concentration gradients inside the reactor (i.e., the assumption of *well stirred*). The outlet concentrations will then be identical to the reactor concentrations, and a simple mole balance yields the CSTR model equation:

$$\frac{d\phi}{dt^*} = \tau_{\text{cstr}} \mathbf{S}(\phi) + \phi_{\text{in}} - \phi. \quad (1.3)$$

The CSTR mean residence time is defined in terms of the inlet flow rate q_{in} and the reactor volume V_{cstr} by

$$\tau_{\text{cstr}} \equiv \frac{V_{\text{cstr}}}{q_{\text{in}}}, \quad (1.4)$$

and the dimensionless time t^* is defined by $t^* \equiv t/\tau_{\text{cstr}}$. At steady state, the left-hand side of (1.3) is zero, and the CSTR model reduces to a system of (non-linear) equations that can be solved for ϕ .

The CSTR model can be derived from the fundamental scalar transport equation (1.28) by integrating the spatial variable over the entire reactor volume. This process results in an integral for the volume-average chemical source term of the form:

$$\int_{V_{\text{cstr}}} \mathbf{S}(\phi(\mathbf{x}, t)) \, d\mathbf{x} = V_{\text{cstr}} \mathbf{S}(\phi(t)), \quad (1.5)$$

where the right-hand side is found by invoking the assumption that ϕ is independent of \mathbf{x} . In the CRE parlance, the CSTR model applies to a reactor that is both *well macromixed* and *well micromixed* (Fig. 1.3). The well macromixed part refers to the fact that a fluid element's location in a CSTR is *independent* of its age.⁸ This fact follows from the well

⁸ The PFR is thus not well macromixed since a fluid element's location in a PFR is a linear function of its age.

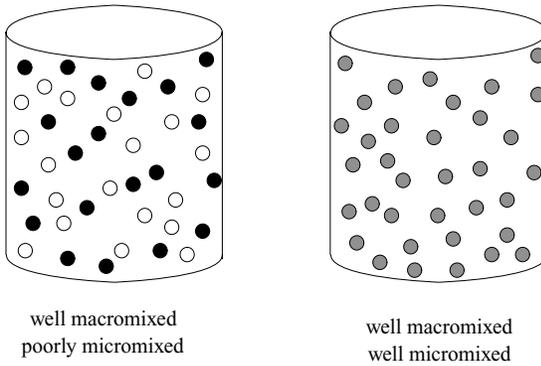


Figure 1.3. Sketch of a poorly micromixed versus a well micromixed CSTR.

stirred assumption, but is not equivalent to it. Indeed, if fluid elements inside the reactor did not interact due to micromixing, then the fluid concentrations ϕ would depend only on the age of the fluid element. Thus, the CSTR model also implies that the reactor is well micromixed.⁹ We will look at the extension of the CSTR model to well macromixed but poorly micromixed systems below.

The applicability of the PFR and CSTR models for a particular set of chemical reactions depends on the characteristic time scales of reaction rates relative to the mixing times. In the PFR model, the only relevant mixing times are the ones that characterize radial dispersion and micromixing. The former will be proportional to the integral time scale of the turbulent flow,¹⁰ and the latter will depend on the inlet flow conditions but, at worst, will also be proportional to the turbulence integral time scale. Thus, the PFR model will be applicable to chemical reaction schemes¹¹ wherein the shortest chemical time scale is greater than or equal to the turbulence integral time scale.

On the other hand, for the CSTR model, the largest time scale for the flow will usually be the *recirculation time*.¹² Typically, the recirculation time will be larger than the largest turbulence integral time scale in the reactor, but smaller than the mean residence time. Chemical reactions with characteristic time scales larger than the recirculation time can be successfully treated using the CSTR model. Chemical reactions that have time scales intermediate between the turbulence integral time scale and the recirculation time should be treated by a CSTR zone model. Finally, chemical reactions that have time scales smaller than the turbulence integral time scale should be described by a micromixing model.

⁹ In the statistical theory of fluid mixing presented in Chapter 3, well macromixed corresponds to the condition that the scalar means $\langle \phi \rangle$ are independent of position, and well micromixed corresponds to the condition that the scalar variances are null. An equivalent definition can be developed from the residence time distribution discussed below.

¹⁰ In Chapter 2, we show that the turbulence integral time scale can be defined in terms of the turbulent kinetic energy k and the turbulent dissipation rate ε by $\tau_u = k/\varepsilon$. In a PFR, τ_u is proportional to $D/\langle U_z \rangle$, where D is the tube diameter.

¹¹ The chemical time scales are defined in Chapter 5. In general, they will be functions of the temperature, pressure, and local concentrations.

¹² Heuristically, the recirculation time is the average time required for a fluid element to return to the impeller region after leaving it.

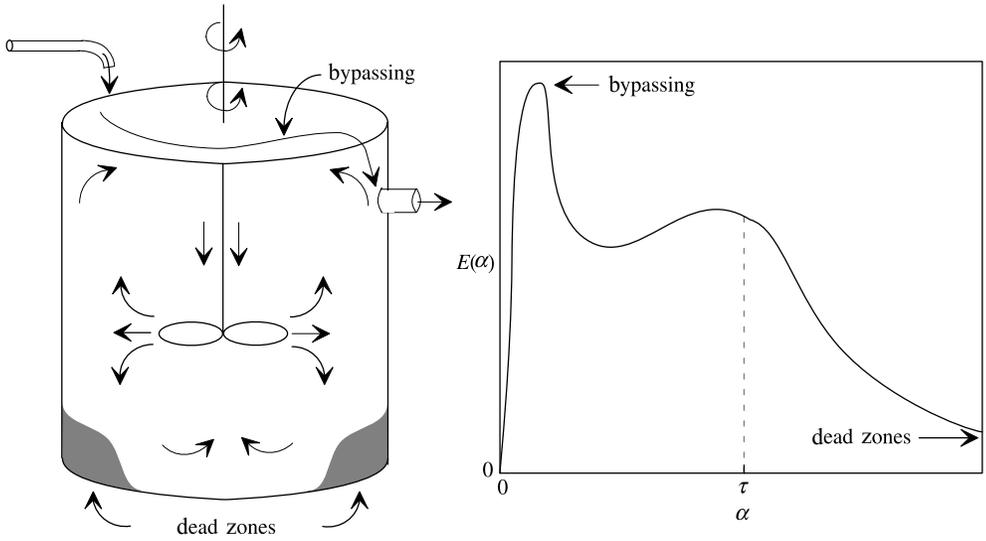


Figure 1.4. Sketch of the residence time distribution (RTD) in a non-ideal reactor.

1.2.2 RTD theory

In the CRE literature, the residence time distribution (RTD) has been shown to be a powerful tool for handling isothermal first-order reactions in arbitrary reactor geometries. (See Nauman and Buffham (1983) for a detailed introduction to RTD theory.) The basic ideas behind RTD theory can be most easily understood in a Lagrangian framework. The residence time of a fluid element is defined to be its age α as it leaves the reactor. Thus, in a PFR, the *RTD function* $E(\alpha)$ has the simple form of a delta function:

$$E_{\text{pfr}}(\alpha) = \delta(\alpha - \tau_{\text{pfr}}), \quad (1.6)$$

i.e., all fluid elements have identical residence times. On the other hand, in a CSTR, the RTD function has an exponential form:¹³

$$E_{\text{cstr}}(\alpha) = \frac{1}{\tau_{\text{cstr}}} \exp\left(-\frac{\alpha}{\tau_{\text{cstr}}}\right). \quad (1.7)$$

RTD functions for combinations of ideal reactors can be constructed (Wen and Fan 1975) based on (1.6) and (1.7). For non-ideal reactors, the RTD function (see example in Fig. 1.4) can be measured experimentally using passive tracers (Levenspiel 1998; Fogler 1999), or extracted numerically from CFD simulations of time-dependent passive scalar mixing.

In this book, an alternative description based on the *joint probability density function* (PDF) of the species concentrations will be developed. (Exact definitions of the joint PDF and related quantities are given in Chapter 3.) The RTD function is in fact the PDF of the fluid-element ages as they leave the reactor. The relationship between the PDF description and the RTD function can be made transparent by defining a fictitious chemical species

¹³ The outflow of a CSTR is a *Poisson process*, i.e., fluid elements are randomly selected regardless of their position in the reactor. The *waiting time* before selection for a Poisson process has an exponential probability distribution. See Feller (1971) for details.

ϕ_τ whose inlet concentration is null, and whose chemical source term is $S_\tau = 1$. Owing to turbulent mixing in a chemical reactor, the PDF of ϕ_τ will be a function of the *composition-space variable* ψ , the spatial location in the reactor \mathbf{x} , and time t . Thus, we will denote the PDF by $f_\tau(\alpha; \mathbf{x}, t)$. The PDF of ϕ_τ at the reactor outlet, $\mathbf{x}_{\text{outlet}}$, is then equal to the *time-dependent* RTD function:

$$E(\alpha, t) = f_\tau(\alpha; \mathbf{x}_{\text{outlet}}, t). \quad (1.8)$$

At steady state, the PDF (and thus the RTD function) will be independent of time. Moreover, the *internal-age distribution* at a point \mathbf{x} inside the reactor is just $I(\alpha; \mathbf{x}, t) = f_\tau(\alpha; \mathbf{x}, t)$. For a *statistically homogeneous* reactor (i.e., a CSTR), the PDF is independent of position, and hence the steady-state internal-age distribution $I(\alpha)$ will be independent of time and position.

One of the early successes of the CRE approach was to show that RTD theory suffices to treat the special case of *non-interacting* fluid elements (Danckwerts 1958). For this case, each fluid element behaves as a *batch reactor*:

$$\frac{d\phi_{\text{batch}}}{d\alpha} = \mathbf{S}(\phi_{\text{batch}}) \quad \text{with} \quad \phi_{\text{batch}}(0) = \phi_{\text{in}}. \quad (1.9)$$

For fixed initial conditions, the solution to this expression is uniquely defined in terms of the age, i.e., $\phi_{\text{batch}}(\alpha)$. The *joint composition PDF* $f_\phi(\psi; \mathbf{x}, t)$ at the reactor outlet is then uniquely defined in terms of the time-dependent RTD distribution:¹⁴

$$f_\phi(\psi; \mathbf{x}_{\text{outlet}}, t) = \int_0^\infty \delta(\psi - \phi_{\text{batch}}(\alpha)) E(\alpha, t) d\alpha, \quad (1.10)$$

where the multi-variable delta function is defined in terms of the product of single-variable delta functions for each chemical species by

$$\delta(\psi - \phi) \equiv \prod_{\beta} \delta(\psi_{\beta} - \phi_{\beta}). \quad (1.11)$$

For the general case of *interacting* fluid elements, (1.9) and (1.10) no longer hold. Indeed, the correspondence between the RTD function and the composition PDF breaks down because the species concentrations inside each fluid element can no longer be uniquely parameterized in terms of the fluid element's age. Thus, for the general case of complex chemistry in non-ideal reactors, a mixing theory based on the composition PDF will be more powerful than one based on RTD theory.

The utility of RTD theory is best illustrated by its treatment of *first-order* chemical reactions. For this case, each fluid element can be treated as a batch reactor.¹⁵ The concentration

¹⁴ At steady state, the left-hand side of this expression has independent variables ψ . For fixed $\psi = \psi^*$, the integral on the right-hand side sweeps over all fluid elements in search of those whose concentrations ϕ_{batch} are equal to ψ^* . If these fluid elements have the same age (say, $\alpha = \alpha^*$), then the joint PDF reduces to $f_\phi(\psi^*; \mathbf{x}_{\text{outlet}}) = E(\alpha^*)$, where $E(\alpha^*) d\alpha^*$ is the fraction of fluid elements with age α^* .

¹⁵ Because the outlet concentrations will not depend on it, micromixing between fluid particles can be neglected. The reader can verify this statement by showing that the micromixing term in the poorly micromixed CSTR and the poorly micromixed PFR falls out when the mean outlet concentration is computed for a first-order chemical reaction. More generally, one can show that the chemical source term appears in closed form in the transport equation for the scalar means.

of a chemical species in a fluid element then depends only on its age through the solution to the batch-reactor model:

$$\frac{d\phi}{d\alpha} = -k\phi \quad \text{with} \quad \phi(0) = \phi_{\text{in}}, \quad (1.12)$$

i.e.,

$$\phi(\alpha) = \phi_{\text{in}} e^{-k\alpha}. \quad (1.13)$$

In RTD theory, the concentrations at the reactor outlet are found by averaging over the ages of all fluid elements leaving the reactor:¹⁶

$$\phi_{\text{out}} = \int_0^{\infty} \phi(\alpha) E(\alpha) d\alpha. \quad (1.14)$$

Thus, for first-order reactions, exact solutions can be found for the outlet concentration, e.g., from (1.13):

$$\left(\frac{\phi_{\text{out}}}{\phi_{\text{in}}} \right)_{\text{pfr}} = e^{-k\tau_{\text{pfr}}} \quad \text{and} \quad \left(\frac{\phi_{\text{out}}}{\phi_{\text{in}}} \right)_{\text{cstr}} = \frac{1}{1 + k\tau_{\text{cstr}}}.$$

For higher-order reactions, the fluid-element concentrations no longer obey (1.9). Additional terms must be added to (1.9) in order to account for micromixing (i.e., local fluid-element interactions due to molecular diffusion). For the poorly micromixed PFR and the poorly micromixed CSTR, extensions of (1.9) can be employed with (1.14) to predict the outlet concentrations in the framework of RTD theory. For non-ideal reactors, extensions of RTD theory to model micromixing have been proposed in the CRE literature. (We will review some of these micromixing models below.) However, due to the non-uniqueness between a fluid element's concentrations and its age, micromixing models based on RTD theory are generally *ad hoc* and difficult to validate experimentally.

1.2.3 Zone models

An alternative method to RTD theory for treating non-ideal reactors is the use of zone models. In this approach, the reactor volume is broken down into well mixed zones (see the example in Fig. 1.5). Unlike RTD theory, zone models employ an Eulerian framework that ignores the age distribution of fluid elements inside each zone. Thus, zone models ignore micromixing, but provide a model for macromixing or large-scale inhomogeneity inside the reactor.

Denoting the *transport rate* of fluid from zone i to zone j by f_{ij} , a zone model can be expressed mathematically in terms of mole balances for each of the N zones:

$$\frac{d\phi^{(i)}}{dt} = \sum_{j=0}^{N+1} (f_{ji}\phi^{(j)} - f_{ij}\phi^{(i)}) + \mathbf{S}(\phi^{(i)}) \quad i = 1, \dots, N. \quad (1.15)$$

¹⁶ For non-interacting fluid elements, the RTD function is thus equivalent to the joint PDF of the concentrations. In composition space, the joint PDF would lie on a one-dimensional sub-manifold (i.e., have a one-dimensional support) parameterized by the age α . The addition of micromixing (i.e., interactions between fluid elements) will cause the joint PDF to spread in composition space, thereby losing its one-dimensional support.

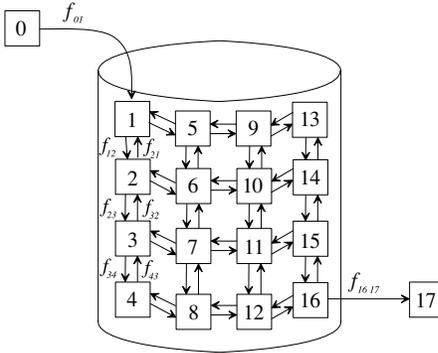


Figure 1.5. Sketch of a 16-zone model for a stirred-tank reactor.

In this expression, the *inlet-zone* ($j = 0$) concentrations are defined by $\phi^{(0)} = \phi_{\text{in}}$, and the *inlet transport rates* are denoted by f_{0i} . Likewise, the *outlet transport rates* are denoted by f_{iN+1} . Thus, by definition, $f_{i0} = f_{N+1i} = 0$.

The transport rates f_{ij} will be determined by the turbulent flow field inside the reactor. When setting up a zone model, various methods have been proposed to extract the transport rates from experimental data (Mann *et al.* 1981; Mann *et al.* 1997), or from CFD simulations. Once the transport rates are known, (1.15) represents a (large) system of coupled ordinary differential equations (ODEs) that can be solved numerically to find the species concentrations in each zone and at the reactor outlet.

The form of (1.15) is identical to the balance equation that is used in finite-volume CFD codes for passive scalar mixing.¹⁷ The principal difference between a zone model and a finite-volume CFD model is that in a zone model the grid can be chosen to optimize the capture of inhomogeneities in the scalar fields *independent* of the mean velocity and turbulence fields.¹⁸ Theoretically, this fact could be exploited to reduce the number of zones to the minimum required to resolve spatial gradients in the scalar fields, thereby greatly reducing the computational requirements.

In general, zone models are applicable to chemical reactions for which local micromixing effects can be ignored. In turbulent flows, the transport rates appearing in (1.15) will scale with the local *integral-scale turbulence frequency*¹⁹ (Pope 2000). Thus, strictly speaking, zone models²⁰ will be applicable to turbulent reacting flows for which the local chemical time scales are all greater than the integral time scale of the turbulence. For chemical reactions with shorter time scales, micromixing can have a significant impact on the species concentrations in each zone, and at the reactor outlet (Weinstein and Adler 1967; Paul and Treybal 1971; Ott and Rys 1975; Bourne and Toor 1977; Bourne *et al.* 1977; Bourne 1983).

¹⁷ In a CFD code, the transport rate will depend on the mean velocity and *turbulent diffusivity* for each zone.

¹⁸ The CFD code must use a grid that also resolves spatial gradients in the mean velocity and turbulence fields. At some locations in the reactor, the scalar fields may be constant, and thus a coarser grid (e.g., a zone) can be employed.

¹⁹ The integral-scale turbulence frequency is the inverse of the turbulence integral time scale. The turbulence time and length scales are defined in Chapter 2.

²⁰ Similar remarks apply for CFD models that ignore sub-grid-scale mixing. The problem of closing the chemical source term is discussed in detail in Chapter 5.

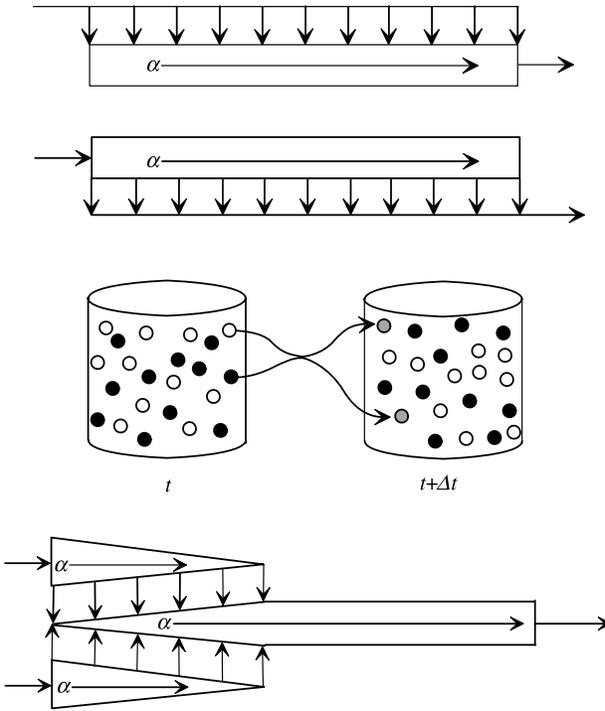


Figure 1.6. Four micromixing models that have appeared in the literature. From top to bottom: maximum-mixedness model; minimum-mixedness model; coalescence-redispersion model; three-environment model.

1.2.4 Micromixing models

Danckwerts (1953) pointed out that RTD theory is insufficient to predict product yields for complex kinetics and noted that a general treatment of this case is extremely difficult (Danckwerts 1957; Danckwerts 1958). Nonetheless, the desire to quantify the degree of segregation in the RTD context has led to a large collection of micromixing models based on RTD theory (e.g., Zwietering 1959; Zwietering 1984). Some of these models are discussed in CRE textbooks (e.g., Fogler 1999). Four examples are shown in Fig. 1.6. Note that these micromixing models do not contain or use any information about the detailed flow field inside the reactor. The principal weakness of RTD-based micromixing models is the lack of a firm physical basis for determining the exchange parameters. We will discuss this point in greater detail in Chapter 3. Moreover, since RTD-based micromixing models do not predict the spatial distribution of reactants inside the reactor, it is impossible to validate fully the model predictions.

Another class of micromixing models is based on *fluid environments* (Nishimura and Matsubara 1970; Ritchie and Tobgy 1979; Mehta and Tarbell 1983a; Mehta and Tarbell 1983b). The basic idea behind these models is to divide *composition space* into a small number of environments that interact due to micromixing. Thus, unlike zone models, which divide up physical space, each environment can be thought of as existing at a particular

spatial location with a certain probability. In some cases, the probabilities are fixed (e.g., equal to the inverse of the number of environments). In other cases, the probabilities evolve due to the interactions between environments. In Section 5.10 we will discuss in detail the general formulation of multi-environment micromixing models in the context of CFD models. Here, we will limit our consideration to two simple models: the *interaction by exchange with the mean* (IEM) model for the poorly micromixed PFR and the IEM model for the poorly micromixed CSTR.

The IEM model for a non-premixed PFR employs two environments with probabilities p_1 and $p_2 = 1 - p_1$, where p_1 is the volume fraction of stream 1 at the reactor inlet. In the IEM model, p_1 is assumed to be constant.²¹ The concentration in environment n is denoted by $\phi^{(n)}$ and obeys

$$\frac{d\phi^{(n)}}{d\alpha} = \frac{1}{t_{\text{iem}}} (\langle\phi(\alpha)\rangle - \phi^{(n)}) + \mathbf{S}(\phi^{(n)}) \quad \text{with} \quad \phi^{(n)}(0) = \phi_{\text{in}}^{(n)}, \quad (1.16)$$

where $\phi_{\text{in}}^{(n)}$ is the inlet concentration to environment n , and t_{iem} is the IEM micromixing time. The first term on the right-hand side of (1.16) is a simple linear model for fluid-particle interactions. In this case, all fluid elements with age α are assumed to interact by exchanging matter with a fictitious fluid element whose concentration is $\langle\phi(\alpha)\rangle$.

By definition, averaging (1.16) with respect to the operator $\langle\cdot\rangle$ (defined below in (1.18)) causes the micromixing term to drop out:²²

$$\frac{d\langle\phi\rangle}{d\alpha} = \langle\mathbf{S}\rangle \quad \text{with} \quad \langle\phi(0)\rangle = \langle\phi_{\text{in}}\rangle. \quad (1.17)$$

Note that in order to close (1.16), the micromixing time must be related to the underlying flow field. Nevertheless, because the IEM model is formulated in a Lagrangian framework, the chemical source term in (1.16) appears in closed form. This is not the case for the chemical source term in (1.17).

The mean concentrations appearing in (1.16) are found by averaging with respect to the *internal-age transfer function*²³ $H(\alpha, \beta)$ and the environments:²⁴

$$\langle\phi(\alpha)\rangle = \sum_{n=1}^2 p_n \int_0^\infty \phi^{(n)}(\beta) H(\alpha, \beta) d\beta. \quad (1.18)$$

For the PFR and the CSTR, $H(\alpha, \beta)$ has particularly simple forms:

$$H_{\text{pfr}}(\alpha, \beta) = \delta(\beta - \alpha) \quad \text{and} \quad H_{\text{cstr}}(\alpha, \beta) = E_{\text{cstr}}(\beta). \quad (1.19)$$

²¹ If p_1 is far from 0.5 (i.e., non-equal-volume mixing), the IEM model yields poor predictions. Alternative models (e.g., the E-model of Baldyga and Bourne (1989)) that account for the evolution of p_1 should be employed to model non-equal-volume mixing.

²² In Chapter 6, this is shown to be a general physical requirement for all micromixing models, resulting from the fact that molecular diffusion in a closed system conserves mass. $\langle\phi(\alpha)\rangle$ is the mean concentration with respect to all fluid elements with age α . Thus, it is a *conditional expected value*.

²³ $H(\alpha, \beta)$ is a *weighting kernel* to generate the contribution of fluid elements with age β to the mean concentration at age α . Similarly, in the transported PDF codes discussed in Chapter 6, a *spatial weighting kernel* of the form $h_{\text{W}}(s)$ appears in the definition of the local mean concentrations.

²⁴ For a CSTR, (1.18) is numerically unstable for small t_{iem} (Fox 1989). For numerical work, it should thus be replaced by an equivalent integro-differential equation (Fox 1991).

Note that the mean concentrations in the PFR are just the volume-averaged concentrations of the two environments with the same age. On the other hand, in the CSTR, the mean concentrations are independent of age (i.e., they are the same at every point in the reactor).

The IEM model can be extended to model unsteady-state stirred reactors (Fox and Villermaux 1990b), and to study micromixing effects for complex reactions using bifurcation theory (Fox and Villermaux 1990a; Fox *et al.* 1990; Fox 1991; Fox *et al.* 1994). Nevertheless, its principal weaknesses when applied to stirred reactors are the need to specify an appropriate micromixing time and the assumption that the mean concentrations are independent of the spatial location in the reactor. However, as discussed in Section 5.10, these shortcomings can be overcome by combining multi-environment micromixing models with CFD models for stirred-tank reactors. A more detailed, but similar, approach based on *transported PDF methods* is discussed in Chapter 6. Both multi-environment CFD models and transported PDF methods essentially combine the advantages of both zone models and micromixing models to provide a more complete description of turbulent reacting flows. An essential ingredient in all approaches for modeling micromixing is the choice of the micromixing time, which we discuss next.

1.2.5 Micromixing time

The micromixing time is a key parameter when modeling fast chemical reactions in non-premixed reactors (Fox 1996a). Indeed, in many cases, the choice of the micromixing time has a much greater impact on the predicted product distribution than the choice of the micromixing model. When combining a CRE micromixing model with a CFD turbulence model, it is thus paramount to understand the relationship between the micromixing time and the scalar dissipation rate.²⁵ The latter is employed in CFD models for scalar mixing based on the transport equation for the *scalar variance*. The relationship between the micromixing time and the scalar dissipation rate is most transparent for the poorly micromixed PFR. We will thus consider this case in detail using the IEM model.

Consider an inert (non-reacting) scalar ϕ in a poorly micromixed PFR. The IEM model for this case reduces to

$$\frac{d\phi^{(n)}}{d\alpha} = \frac{1}{t_{iem}} (\langle\phi(\alpha)\rangle - \phi^{(n)}) \quad \text{with } n = 1, 2, \quad (1.20)$$

where

$$\langle\phi(\alpha)\rangle = p_1\phi^{(1)}(\alpha) + p_2\phi^{(2)}(\alpha). \quad (1.21)$$

Since the inlet concentrations will have no effect on the final result, for simplicity we let $\phi^{(1)}(0) = 0$ and $\phi^{(2)}(0) = 1$. Applying (1.18) to (1.20), it is easily shown that the scalar mean is constant and given by $\langle\phi(\alpha)\rangle = p_2$.

²⁵ The scalar dissipation rate is defined in Chapter 3.

The next step is to derive an expression for the scalar variance defined by

$$\langle \phi'^2(\alpha) \rangle \equiv \langle \phi^2(\alpha) \rangle - \langle \phi(\alpha) \rangle^2 \quad (1.22)$$

wherein

$$\langle \phi^2(\alpha) \rangle = \sum_{n=1}^2 p_n (\phi^{(n)}(\alpha))^2. \quad (1.23)$$

Differentiating (1.22) with respect to α and substituting (1.20) leads to

$$\frac{d\langle \phi'^2 \rangle}{d\alpha} = -\frac{2}{t_{\text{iem}}} \langle \phi'^2 \rangle. \quad (1.24)$$

In Section 3.2, we show that under the same conditions the right-hand side of (1.24) is equal to the negative scalar dissipation rate ((3.45), p. 70). Thus, the micromixing time is related to the scalar dissipation rate ε_ϕ and the scalar variance by

$$t_{\text{iem}} = \tau_\phi \equiv \frac{2\langle \phi'^2 \rangle}{\varepsilon_\phi}. \quad (1.25)$$

Choosing the micromixing time in a CRE micromixing model is therefore equivalent to choosing the scalar dissipation rate in a CFD model for scalar mixing.

In the CRE literature, turbulence-based micromixing models have been proposed that set the micromixing time proportional to the Kolmogorov time scale:

$$t_{\text{iem}} \propto \left(\frac{\nu}{\varepsilon} \right)^{1/2}, \quad (1.26)$$

where ν is the kinematic viscosity of the fluid, and ε is the turbulent dissipation rate. As discussed in detail in Chapter 3, this choice is only valid under *very limited* inlet conditions. In fact, the micromixing time will be strongly dependent on the inlet conditions of the scalar field and the underlying turbulence fields. In CFD models for scalar mixing, the micromixing time is usually found either by assuming that the scalar dissipation rate is controlled by the *rate of scalar energy transfer* from large to small scales (the so-called *equilibrium model*), or by solving a transport equation for ε . We will look at both approaches in Chapters 3 and 4.

1.3 Fluid-mechanical approach

The FM approach to modeling turbulent reacting flows had as its initial focus the description of turbulent combustion processes (e.g., Chung 1969; Chung 1970; Flagan and Appleton 1974; Bilger 1989). In many of the early applications, the details of the chemical reactions were effectively ignored because the reactions could be assumed to be in local chemical equilibrium.²⁶ Thus, unlike the early emphasis on slow and finite-rate reactions

²⁶ In other words, all chemical reactions are assumed to occur much faster than micromixing.

in the CRE literature, much of the early FM literature on reacting flows emphasized the modeling of the turbulent flow field and the effects of density changes due to chemical reactions. However, more recently, the importance of finite-rate reactions in combustion processes has become clear. This, in turn, has led to the development of FM approaches that can handle complex chemistry but are numerically tractable (Warnatz *et al.* 1996; Peters 2000).

Like CRE micromixing models, the goal of current FM approaches is the accurate treatment of the chemical source term and molecular mixing. As a starting point, most FM approaches for turbulent reacting flows can be formulated in terms of the joint PDF of the velocity and the composition variables. Thus, many experimental and theoretical studies have reported on velocity and concentration fluctuation statistics in simple canonical flows (Corrsin 1958; Corrsin 1961; Toor 1962; Lee and Brodkey 1964; Keeler *et al.* 1965; Vassilatou and Toor 1965; Brodkey 1966; Gegner and Brodkey 1966; Lee 1966; Corrsin 1968; Toor 1969; Torrest and Ranz 1970; Mao and Toor 1971; Gibson and Libby 1972; Lin and O'Brien 1972; Dopazo and O'Brien 1973; Lin and O'Brien 1974; Dopazo and O'Brien 1976; Hill 1976; Breidenthal 1981; Bennani *et al.* 1985; Lundgren 1985; Koochesfahani and Dimotakis 1986; Hamba 1987; Komori *et al.* 1989; Bilger *et al.* 1991; Guiraud *et al.* 1991; Komori *et al.* 1991a; Komori *et al.* 1991b; Brown and Bilger 1996). In Chapters 2 and 3, we review the statistical description of turbulent flows and turbulent scalar mixing. In the remainder of this section, we give a brief overview of the FM approach to modeling turbulent reacting flows. In the following section, we will compare the similarities and differences between the CRE and FM approaches.

1.3.1 Fundamental transport equations

For the constant-density flows considered in this work,²⁷ the fundamental governing equations are the Navier–Stokes equation for the fluid velocity \mathbf{U} (Bird *et al.* 2002):

$$\frac{\partial U_i}{\partial t} + U_j \frac{\partial U_i}{\partial x_j} = \nu \frac{\partial^2 U_i}{\partial x_j \partial x_j} - \frac{1}{\rho} \frac{\partial p}{\partial x_i}, \quad (1.27)$$

and the reacting scalar transport equation (ϕ_α represents a chemical species concentration or enthalpy):

$$\frac{\partial \phi_\alpha}{\partial t} + U_j \frac{\partial \phi_\alpha}{\partial x_j} = \Gamma_\alpha \frac{\partial^2 \phi_\alpha}{\partial x_j \partial x_j} + S_\alpha(\phi). \quad (1.28)$$

In interpreting these expressions, the usual summation rules for roman indices apply, e.g., $a_i b_i = a_1 b_1 + a_2 b_2 + a_3 b_3$. Note that the scalar fields are assumed to be *passive*, i.e., ϕ does not appear in (1.27).

The fluid density appearing in (1.27) is denoted by ρ and is assumed to be constant. The molecular-transport coefficients appearing in the governing equations are the kinematic

²⁷ Although this choice excludes combustion, most of the modeling approaches can be directly extended to non-constant-density flows with minor modifications.

viscosity ν , and the molecular and thermal diffusivities Γ_α for the chemical species and enthalpy fields. The pressure field p appearing on the right-hand side of (1.27) is governed by a Poisson equation:

$$\nabla^2 p = -\rho \frac{\partial U_i}{\partial x_j} \frac{\partial U_j}{\partial x_i}. \quad (1.29)$$

This expression is found from (1.27) using the continuity equation for a constant-density flow:

$$\nabla \cdot \mathbf{U} = 0. \quad (1.30)$$

The last term on the right-hand side of (1.28) is the chemical source term. As will be seen in Chapter 5, the chemical source term is often a complex, non-linear function of the scalar fields ϕ , and thus solutions to (1.28) are very different than those for the *inert*-scalar transport equation wherein \mathbf{S} is null.

1.3.2 Turbulence models

Under the operating conditions of most industrial-scale chemical reactors, the solution to (1.27) will be *turbulent* with a large range of length and time scales (Bischoff 1966; McKelvey *et al.* 1975; Brodkey 1984; Villermaux 1991). As a consequence of the complexity of the velocity field, chemical-reactor models based on solving (1.27) directly are computationally intractable. Because of this, in its early stages of development, the FM approach for turbulent mixing was restricted to describing canonical turbulent flows (Corrsin 1951a; Corrsin 1951b; Corrsin 1957; Gibson and Schwarz 1963a; Gibson and Schwarz 1963b; Lee and Brodkey 1964; Nye and Brodkey 1967a; Nye and Brodkey 1967b; Gibson 1968a; Gibson 1968b; Grant *et al.* 1968; Christiansen 1969; Gibson *et al.* 1970), and thus had little impact on CRE models for industrial-scale chemical reactors. However, with the advances in computing technology, CFD has become a viable tool for simulating industrial-scale chemical reactors using *turbulence models* based on the statistical theory of turbulent flows.

The potential economic impact of CFD in many engineering disciplines has led to considerable research in developing Reynolds-averaged Navier–Stokes (RANS) turbulence models (Daly and Harlow 1970; Launder and Spalding 1972; Launder 1991; Hanjalić 1994; Launder 1996) that can predict the mean velocity (\mathbf{U}), turbulent kinetic energy k , and the turbulent dissipation rate ε in high-Reynolds-number turbulent flows.²⁸ These and more sophisticated models are now widely available in commercial CFD codes, and are routinely employed for reactor design in the chemical process industry. For completeness, we review some of the most widely used turbulence models in Chapter 4. A more thorough discussion of the foundations of turbulence modeling can be found in Pope (2000).

Similarly, turbulent scalar transport models based on (1.28) for the case where the chemical source term is null have been widely studied. Because (1.28) in the absence

²⁸ The experienced reader will recognize these CFD models as the so-called RANS turbulence models.

of chemical reactions is linear in the scalar variable, CFD models for the mean scalar field closely resemble the corresponding turbulence models for k and ε . In Chapter 3, the transport equation for the scalar mean is derived starting from (1.28) using Reynolds averaging. For inert-scalar turbulent mixing, the closure problem reduces to finding an appropriate model for the *scalar flux*. In most CFD codes, the scalar flux is found either by a gradient-diffusion model or by solving an appropriate transport equation. Likewise, scalar fluctuations can be characterized by solving the transport equation of the scalar variance (see Chapter 3). For *reacting-scalar* turbulent mixing, the chemical source term poses novel, and technically more difficult, closure problems.

1.3.3 Chemical source term

Despite the progress in CFD for inert-scalar transport, it was recognized early on that the treatment of turbulent *reacting* flows offers unique challenges (Corrsin 1958; Danckwerts 1958). Indeed, while turbulent transport of an inert scalar can often be successfully described by a small set of *statistical moments* (e.g., $\langle \mathbf{U} \rangle$, k , ε , $\langle \phi \rangle$, and $\langle \phi'^2 \rangle$), the same is not true for scalar fields, which are strongly coupled through the chemical source term in (1.28). Nevertheless, it has also been recognized that because the chemical source term depends only on the *local* molar concentrations \mathbf{c} and temperature T :

$$\mathbf{S}(\phi), \quad \text{where} \quad \phi^T = (c_A, c_B, \dots, T),$$

knowledge of the one-point, one-time composition PDF $f_\phi(\psi; \mathbf{x}, t)$ at all points in the flow will suffice to predict the mean chemical source term $\langle \mathbf{S} \rangle$, which appears in the reacting-scalar transport equation for the scalar means $\langle \phi \rangle$ (Chung 1976; O'Brien 1980; Pope 1985; Kollmann 1990).

As discussed in Chapter 2, a fully developed turbulent flow field contains flow structures with length scales much smaller than the grid cells used in most CFD codes (Daly and Harlow 1970).²⁹ Thus, CFD models based on *moment methods* do not contain the information needed to predict $f_\phi(\psi; \mathbf{x}, t)$. Indeed, only the direct numerical simulation (DNS) of (1.27)–(1.29) uses a fine enough grid to resolve completely all flow structures, and thereby avoids the need to predict $f_\phi(\psi; \mathbf{x}, t)$. In the CFD literature, the small-scale structures that control the chemical source term are called sub-grid-scale (SGS) fields, as illustrated in Fig. 1.7.

Heuristically, the SGS distribution of a scalar field $\phi(\mathbf{x}, t)$ can be used to *estimate* the composition PDF by constructing a histogram from all SGS points within a particular CFD grid cell.³⁰ Moreover, because the important statistics needed to describe a scalar field (e.g., its expected value $\langle \phi \rangle$ or its variance $\langle \phi'^2 \rangle$) are nearly constant on sub-grid

²⁹ Only direct numerical simulation (DNS) resolves all scales (Moin and Mahesh 1998). However, DNS is computationally intractable for chemical reactor modeling.

³⁰ The reader familiar with the various forms of averaging (Pope 2000) will recognize this as a spatial average over a locally statistically homogeneous field.

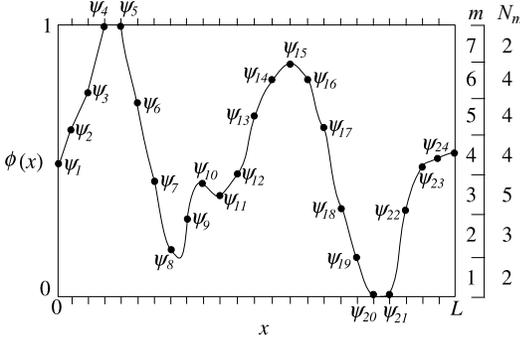


Figure 1.7. Sketch of sub-grid-scale (SGS) distribution of ϕ .

scales, the SGS field can be considered *statistically homogeneous*. This implies that all points sampled from the same CFD grid cell are statistically equivalent, i.e., sampled from the same composition PDF.

As an example of estimating a scalar PDF, consider a *bounded*, one-dimensional scalar field $\phi \in [0, 1]$ defined on $x \in [0, L]$, where L is the CFD grid size as shown in Fig. 1.7. In a CFD calculation, only $\phi(0)$ and $\phi(L)$ would be computed (or, more precisely, the mean values $\langle \phi(0) \rangle$ and $\langle \phi(L) \rangle$ at the grid points). However, if $\phi(x)$ were somehow available for all values of x , a histogram could be constructed as follows:

- (i) Choose a fine grid with spacing $l \ll L$, and let $N = 1 + \text{integer}(L/l)$. Sample $\phi(x)$ on the fine grid:

$$\psi_1 = \phi(0), \psi_2 = \phi(l), \psi_3 = \phi(2l), \dots, \psi_N = \phi((N-1)l).$$

- (ii) Use the samples (ψ_1, \dots, ψ_N) to construct a histogram for ϕ :
 - (a) Construct M bins in composition space $\psi \in [0, 1]$ with spacing $\Delta = 1/M$.
 - (b) Count the number of samples N_m that fall in bin $m \in 1, \dots, M$.
 - (c) Define the value of the histogram at bin m by

$$h(m\Delta) \equiv \frac{N_m}{N\Delta}. \quad (1.31)$$

(Note that in anticipation of considering the histogram as an approximation of the PDF of ϕ , $h(\psi)$ has been normalized so that its integral over composition space is unity.)

- (iii) The histogram can then be plotted versus the mid-point value for each bin as shown in Fig. 1.8.

In the limit where $l \rightarrow 0$, the number of samples N will become very large, and the bin spacing Δ can be decreased while keeping N_m large enough to control statistical fluctuations. The histogram then becomes nearly continuous in ψ and can be used to

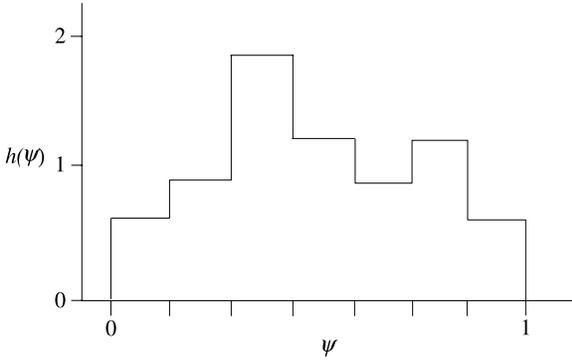


Figure 1.8. Histogram for sub-grid-scale distribution of ϕ based on 24 samples and seven bins.

estimate the PDF of ϕ :

$$\lim_{N, M \rightarrow \infty} h(m\Delta) \rightarrow \hat{f}_\phi(\psi). \quad (1.32)$$

The true PDF $f_\phi(\psi)$ is defined axiomatically (see Chapter 3), but can be thought of as representing all possible realizations of $\phi(x)$ generated with the same flow conditions (i.e., an *ensemble*). Because $\hat{f}_\phi(\psi)$ has been found based on a single realization, it may or may not be a good approximation for $f_\phi(\psi)$, depending on how well the single realization represents the entire ensemble. Generally speaking, in a turbulent flow the latter will depend on the value of the *integral scale* of the quantity of interest relative to the grid spacing L . For a turbulent scalar field, the integral scale L_ϕ is often approximately equal to L , in which case $\hat{f}_\phi(\psi)$ offers a poor representation of $f_\phi(\psi)$. However, for statistically stationary flows, the estimate can be improved by collecting samples at different times.³¹

For turbulent reacting flows, we are usually interested in chemical reactions involving multiple scalars. As for a single scalar, a histogram can be constructed from multiple scalar fields (Fig. 1.9). For example, if there are two reactants A and B, the samples will be bi-variate:

$$\begin{aligned} \psi_1 &= (\phi_A(0), \phi_B(0)), \\ \psi_2 &= (\phi_A(l), \phi_B(l)), \\ \psi_3 &= (\phi_A(2l), \phi_B(2l)), \\ &\vdots \\ \psi_N &= (\phi_A((N-1)l), \phi_B((N-1)l)). \end{aligned}$$

The resultant histogram is also bi-variate, $h_{A,B}(m_A\Delta_A, m_B\Delta_B)$, and can be represented by a contour plot, as shown in Fig. 1.10.

³¹ This procedure is widely used when extracting statistical estimates from DNS data.

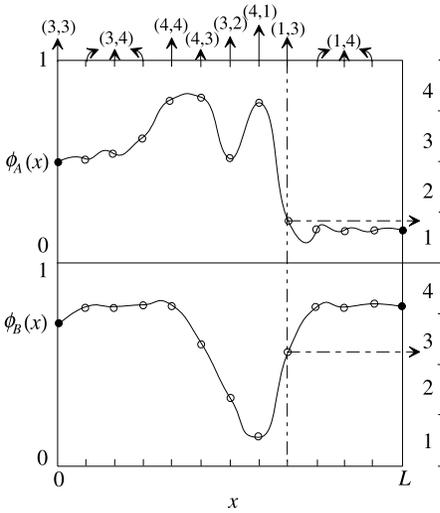


Figure 1.9. Sketch of sub-grid-scale distribution of ϕ_A and ϕ_B . The bin numbers for each sample point are given at the top of the figure.

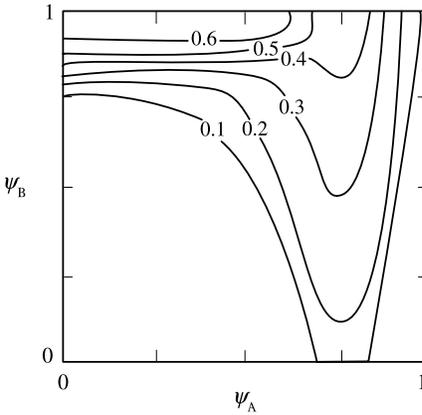
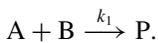


Figure 1.10. Contour plot of the joint histogram for ϕ_A and ϕ_B .

Likewise, in the limit of large numbers of samples and bins, the bi-variate histogram can be used to compute an estimate for the joint PDF of ϕ_A and ϕ_B :

$$\lim_{N, M_A, M_B \rightarrow \infty} h_{A,B}(\psi_A, \psi_B) \rightarrow \hat{f}_{A,B}(\psi_A, \psi_B). \tag{1.33}$$

We shall see in Chapter 5 that knowledge of $f_{A,B}(\psi_A, \psi_B)$ suffices to close the chemical source term for the isothermal, second-order reaction



The procedure presented above can be easily extended to estimate the joint PDF of a vector of K composition variables $f_\phi(\psi)$. For example, the mean chemical source term $\langle S \rangle$ inside a CFD grid cell can be estimated by sampling the chemical source term at every

point on a finer grid:

$$\begin{aligned}\mathbf{S}_1 &= \mathbf{S}(\psi_1), \\ \mathbf{S}_2 &= \mathbf{S}(\psi_2), \\ \mathbf{S}_3 &= \mathbf{S}(\psi_3), \\ &\vdots \\ \mathbf{S}_N &= \mathbf{S}(\psi_N); \end{aligned}$$

and summing over all samples:

$$\begin{aligned}\langle \mathbf{S} \rangle &\equiv \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \mathbf{S}(\psi) f_\phi(\psi) d\psi \\ &\approx \sum_{m_1=1}^{M_1} \cdots \sum_{m_K=1}^{M_K} \mathbf{S}(m_1 \Delta_1, \dots, m_K \Delta_K) h(m_1 \Delta_1, \dots, m_K \Delta_K) \Delta_1 \cdots \Delta_K \\ &\approx \frac{1}{N} \sum_{n=1}^N \mathbf{S}(\psi_n). \end{aligned} \quad (1.34)$$

The last term in (1.34) follows by approximating \mathbf{S} evaluated at the bin center by its value at a sample point contained in the bin. In the limit where the fine grid becomes infinitely fine, the last term is just the spatial-average chemical source term:

$$\langle \mathbf{S} \rangle_L = \int_0^L \mathbf{S}(\phi(x)) dx = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{n=1}^N \mathbf{S}(\psi_n). \quad (1.35)$$

Note that (1.34) defines the mean chemical source term in terms of $f_\phi(\psi)$, and that the latter contains considerably less information than the original scalar fields $\phi(x)$.³²

In summary, the FM approach to turbulent reacting flows is closely connected (either directly or indirectly) with the determination of the joint composition PDF. As is true for turbulent flows (Pope 2000), statistical models for turbulent reacting flows are best derived axiomatically (e.g., in terms of $\langle \mathbf{S} \rangle$ instead of $\langle \mathbf{S} \rangle_L$). In the examples given above, we assumed that the SGS scalar fields were known, and thus were able to estimate the composition joint PDF using a histogram. The challenge posed in the FM approach to turbulent reacting flows is thus to derive adequate representations for the mean chemical source term consistent with known theoretical constraints and experimental observations *without direct knowledge of the SGS scalar fields*. For this purpose, many *one-point* models (with widely differing degrees of generality) have been proposed and successfully implemented. In Chapter 5, the most general and widely employed models are discussed in some detail. A common feature of all one-point models for turbulent reacting flows is the need for a description of molecular mixing.

³² For example, all information is lost concerning the relative spatial locations of two random samples. As discussed in Chapter 2, this fact implies that all information concerning the spatial derivatives of the scalar fields is lost when the scalar field is described by its *one-point* joint PDF.

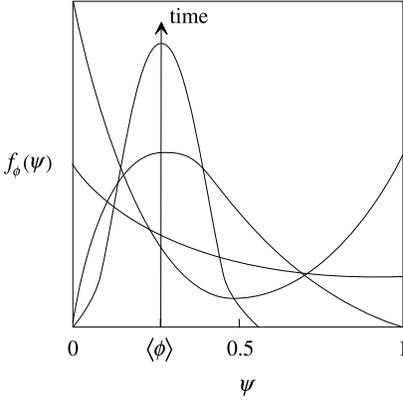


Figure 1.11. A non-premixed scalar PDF as a function of time for inert-scalar mixing. Note that at very short times the PDF is bi-modal since all molecular mixing occurs in thin diffusion layers between regions of pure fluid where $\phi = 0$ or 1. On the other hand, for large times, the scalar PDF is nearly Gaussian.

1.3.4 Molecular mixing

As seen above, the mean chemical source term is intimately related to the PDF of the *concentration fluctuations*. In non-premixed flows, the rate of decay of the concentration fluctuations is controlled by the scalar dissipation rate. Thus, a critical part of any model for chemical reacting flows is a description of how molecular diffusion works to damp out concentration fluctuations at the SGS level.

As an example, consider the Lagrangian formulation of (1.28):

$$\frac{d\phi_\alpha^*}{dt} = \langle \Gamma_\alpha \nabla^2 \phi_\alpha | \phi = \phi^* \rangle + S_\alpha(\phi^*). \quad (1.36)$$

The first term on the right-hand side is the expected value of the scalar Laplacian *conditioned* on the scalars having values ϕ^* .³³ An example of the time evolution of the *conditional scalar Laplacian*, corresponding to the scalar PDF in Fig. 1.11, is plotted in Fig. 1.12 for an initially non-premixed inert-scalar field. The closure of the conditional scalar Laplacian is discussed in Chapter 6. For the time being, it suffices to note the similarity between (1.36) and the IEM model, (1.16). Indeed, the IEM model is a closure for the conditional scalar Laplacian, i.e.,

$$\langle \Gamma_\alpha \nabla^2 \phi_\alpha | \phi = \phi^* \rangle = \frac{1}{\tau_\phi} (\langle \phi \rangle - \phi^*), \quad (1.37)$$

which is widely employed in transported PDF simulations of turbulent reacting flows.³⁴

In other closures for the chemical source term, a model for the *conditional scalar dissipation rate* $\langle \epsilon_\phi | \phi = \psi \rangle$ is required. (An example is plotted in Fig. 1.13 for the scalar PDF shown in Fig. 1.11.) Like the conditional scalar Laplacian, the conditional scalar

³³ Conditional expectations are defined in Chapter 2.

³⁴ Note that all terms in (1.37) can be directly extracted from DNS data for turbulent-scalar mixing. Thus, unlike the CRE approach, the FM approach allows for the direct validation of micromixing models.

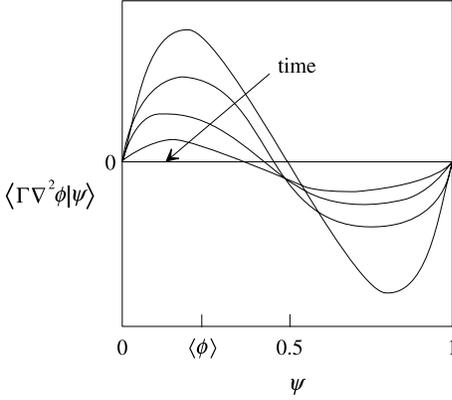


Figure 1.12. The conditional scalar Laplacian $\langle \Gamma \nabla^2 \phi | \psi \rangle$ for the scalar PDF in Fig. 1.11. Note that at very short times $\langle \Gamma \nabla^2 \phi | \psi = 0.5 \rangle = 0$, since all molecular mixing occurs in thin diffusion layers between regions of pure fluid where $\phi = 0$ or 1. On the other hand, for large times, $\langle \Gamma \nabla^2 \phi | \psi = \langle \phi \rangle \rangle = 0$. In this limit, the scalar field is nearly Gaussian, and the conditional scalar Laplacian can be accurately described by the IEM model.

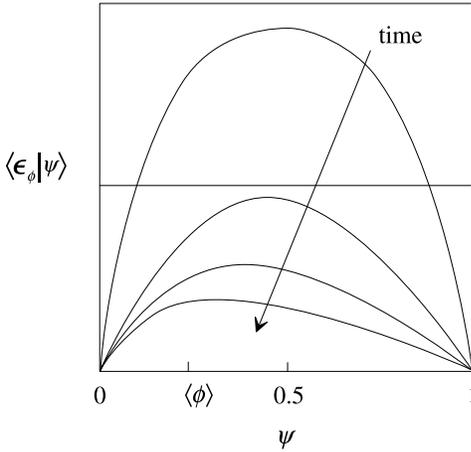


Figure 1.13. The conditional scalar dissipation rate $\langle \epsilon_\phi | \psi \rangle$ for the scalar PDF in Fig. 1.11.

dissipation rate can be extracted from DNS data for model validation. For non-premixed reacting flows, the effects of chemical reactions on the molecular mixing terms are generally ignored (e.g., τ_ϕ in (1.37) is assumed to be the same for all scalars). Nevertheless, one of the great advantages of the FM approach is that assumptions of this type can be verified using DNS data for turbulent reacting flows. Indeed, since the advent of DNS, significant improvements in molecular mixing models have resulted due to model validation studies.

1.4 Relationship between approaches

The relationship between the CRE approach and the FM approach to modeling turbulent reacting flows is summarized in Table 1.1. Despite the obvious and significant differences