COMPUTATIONS OF TURBULENT COMBUSTION: PROGRESS AND CHALLENGES

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We review the significant progress that has been made in the development and use of turbulent combustion models applicable to practical combustion devices. Recent work has focused on the development of methods that can treat finite-rate kinetics in a realistic yet tractable way, so that local extinction and related phenomena can be studied. Direct numerical simulation cannot be used for this purpose, because it is computationally intractable; and the potential of large-eddy simulation is far from clear because combustion reactions give rise to a severe closure problem. PDF methods, on the other hand, overcome the major closure problems, and they have shown to be tractable for complex flows and with realistic finite-rate kinetics.

A simple explanation of pdf methods is presented. It is shown that the single modelled equation for the joint pdf of velocity, dissipation and composition provides a closure for turbulent combustion. Reaction and convection are treated exactly, while the modelling is performed in a Lagrangian setting, by constructing deterministic or stochastic models for the evolution of fluid-particle properties. Examples of recent pdf calculations are described, including those based on four-step mechanisms for methane. Extension of pdf methods to include composition gradients is discussed, with a view to improving the modelling of molecular diffusion.

Introduction

In turbulent combustion—as in most fields of study—the ultimate scientific objective is to obtain a tractable quantitative theory. Given the complexity of the problem, it is inevitable that specific calculations based on such a theory will entail sizeable computations. Because of the remarkable advances over the last 20 years in chemical kinetics, laminar flame theory, laser diagnostics, turbulence modelling and computer technology, the prospect of attaining a tractable quantitative theory of turbulent combustion now appears quite realistic.

Attention is restricted to the central topic of single-phase (gaseous) turbulent combustion. We use the term turbulent combustion model to describe any computational method applicable to the general case of statistically three-dimensional time-dependent flows, and which calculates, at a minimum, the mean velocity and composition fields.

The purpose of this lecture is to illustrate the abilities and shortcomings of current turbulent combustion models, and to identify the course of future research most likely to lead to an accurate, tractable theory.

While the motivation given above is purely scientific, much of the impetus for research in combustion stems from the practical importance of turbulent combustion in furnaces, boilers, gas-turbines and internal combustion engines. In the next section, we briefly review some uses of turbulent combustion models in industry. It is clear that these models are now an accepted design tool, and that their importance will increase with time.

In the third section, the theoretical and computational problems posed by turbulent combustion are examined, and different approaches are discussed. It is impracticable—now or in the future—to use direct numerical simulation (DNS) to calculate the flow within practical combustion devices. PDF methods appear to be the best approach available since they completely overcome the closure problem associated with nonlinear reaction rates. In large-eddy simulations (LES) this closure problems remains, and hence for turbulent combustion LES does not appear to be a competitive approach—as it may be for inert flows.

PDF methods are examined in more detail in the fourth section, where examples of recent calculations are given.

Through their choice of topic, the two previous lecturers at this Colloquium—Bilger and Peters—have agreed on one point: the most important theoretical issue in turbulent combustion at present is the coupling between reaction and diffusive processes on the smallest scales. This issue is ad-
dressed in the fifth section where it is shown that flamelet and non-flamelet notions can be reconciled within the pdf approach.

Modelling Turbulent Combustion in Industry

Current Usage:

Are turbulent combustion models useful in the design of combustion devices? No longer does this question have to be asked. For, through its actions, industry has answered: yes. Without exception, every major gas-turbine company uses turbulent combustion models as part of the design procedure (e.g. Refs. 3–6). Similarly, there is substantial effort and progress in applying turbulent combustion models to internal combustion engines (e.g. Refs. 7–9).

Generally, the combustion in gas turbines and furnaces is idealized as a turbulent diffusion (or nonpremixed) flame. The turbulent combustion models currently in use in these applications—described by, for example, Jones & Whitelaw10 and Correa & Shyy9—are based on models developed in the early 1970’s. The turbulence is described by the k-ε model,11,12 and modelled equations are solved for the mean and variance of the mixture fraction.13–16 Equilibrium chemistry is assumed, so that all thermochemical statistics can be obtained from the probability density function (pdf) of mixture fraction. An assumption is made about the shape of this pdf—e.g. that it is a beta-function distribution—so that at any point the pdf is uniquely determined by the calculated mean and variance of the mixture fraction. In essence, this formulation reduces nonpremixed combustion to a mixing problem: the calculated fields are independent of all reaction rates.

The combustion in a homogeneously-charged spark-ignition engine is idealized as a turbulent premixed flame. These flames have proved to be much more difficult to model than diffusion flames.17,18 The main reason for this increased difficulty is that turbulent premixed combustion cannot as simply be reduced to a mixing problem. Consequently, while several models are in use,8,19–21 none can be regarded as being as satisfactory as the mixture-fraction formulation for diffusion flames.

For both premixed and nonpremixed combustion, the models currently in use are not as accurate as desirable, and they do not address all of the issues—especially those related to finite-rate kinetics. Nevertheless, they have proved their worth by shortening the expensive development procedure, and by providing insight into the flow and mixing within the combustion device. And the cost-effectiveness of using turbulent combustion modelling can only increase with time, as the models improve, as computers become more powerful and accessible, and as empirical testing becomes more costly.

Although the basic models were developed, typically, 15 years ago, it should be realized that significant obstacles—both technical and sociological—have had to be overcome to reach the current level of industrial application. The geometries of practical combustion devices are quite complicated, and have required the development of specialized grid-generation procedures, and of numerical methods for non-Cartesian grids.5–10 Since the flow fields are invariably three-dimensional, computer graphics have had to be developed so that the calculated flow fields can be understood. And finally, the adoption of turbulent combustion models in industry has required gaining the long-term support of management, and its acceptance by designers. These substantial obstacles having been largely overcome, there is now a relatively short and certain path between the development of an improved turbulent combustion model and the consequent benefits to the design process.

Improvements Required:

To meet all practical design needs, current turbulent combustion models need to be improved in the following respects:

i) generality,
ii) finite-rate kinetics,
iii) accuracy of turbulence modelling,
iv) incorporation of additional effects.

Most models are applicable either to diffusion flames (with a single fuel stream and a single air stream) or to premixed flames (in which the reactants are thermochemically uniform). Many important combustion processes are not well approximated by these idealizations. Examples are: staged combustion; piloted diffusion flames; stratified charge engines; and inhomogeneously premixed flames (as may occur in two-stroke engines).

The major improvement currently being sought is the ability to handle realistic finite-rate chemical kinetics. There are two motivations. The first is to calculate the effects of “slow” reactions, such as the production of NOx and soot, or the post-flame oxidation of CO. The second—and much more difficult—objective is to calculate ignition, extinction and related phenomena.

These first two issues—generality and finite-rate kinetics—form the central theme of this lecture. The last two issues are not considered beyond the following brief comments.

The k-ε model has several known defects—for example its considerable inaccuracy when applied to swirling flows.22 Reynolds-stress closures are making steady progress23,24 and while not all of the
difficulties have been resolved, there do not appear to be any insurmountable obstacles lying on the path of further progress. Any improvements gained in Reynolds-stress closures can immediately by incorporated in pdf methods, to yield, presumably, a corresponding improvement in the accuracy of the calculated mean velocity and Reynolds-stress fields.

The central problem considered here is the interaction between turbulence and chemistry in gaseous flames. One should not lose sight, however, of the fact that there are several additional effects that may be of major importance in practical combustion devices. These include: sprays, soot, radiation, and compressibility in high-speed flows. Thus, in practice, the basic "turbulent combustion models" considered here may be augmented by additional models for these other effects.

**Approaches**

In this section, several different approaches to the problem of turbulent combustion are briefly reviewed in order to identify the major difficulties and the type of approach that can overcome them.

It is appropriate to start by asking the question: can turbulent combustion be computed from first principles? The first step towards answering this question is to consider the fundamental conservation equations.

**Governing Equations:**

For simplicity of exposition, we consider a low Mach number flow, neglect radiation, and assume that the reference pressure $p_0$ is constant (as it is in the steady operation of any combustion device). Then at any position $\mathbf{x}$ and time $t$ the thermochemical state of the fluid is uniquely determined by $p_0$ and a set of $\sigma$ composition variables $\phi(\mathbf{x}, t) = \{\phi_\alpha(\mathbf{x}, t), \alpha = 1, 2, \ldots, \sigma\}$. These variables can be taken to be the mass fractions of the chemical species, and the enthalpy. Thus there are equations of state, e.g.

$$
\rho(\mathbf{x}, t) = \rho(\phi(\mathbf{x}, t), p_0) \quad \text{and} \\
T(\mathbf{x}, t) = T(\phi(\mathbf{x}, t), p_0),
$$

relating the density, temperature and any other thermochemical property to the compositions. (Henceforth the dependence of such quantities on $p_0$ is not shown explicitly.)

The conservation of mass, momentum, chemical species and energy lead to the following set of equations:

$$
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho U_i) = 0,
$$

$$
\rho \frac{\partial U_i}{\partial t} = \frac{\partial \tau_{ij}}{\partial x_j} - \frac{\partial p}{\partial x_i} + \rho g_i,
$$

$$
\rho \frac{D \phi_\alpha}{Dt} = - \frac{\partial \bar{\phi}_\alpha}{\partial x_i} + \rho \dot{S}_\alpha,
$$

where the material derivative is

$$
\frac{D}{Dt} = \frac{\partial}{\partial t} + U_i \frac{\partial}{\partial x_i},
$$

$\mathcal{U}(\mathbf{x}, t)$ is the fluid velocity, $p(\mathbf{x}, t)$ is the pressure, $\mathbf{g}$ is the body force, $\tau_{ij}$ is the stress tensor, and $\bar{J}_\alpha$ is the diffusive flux of $\phi_\alpha$. It is important to recognize that the all-important source terms, $S_\alpha$, which are combinations of elementary reaction rates—are uniquely determined by the thermochemical state. Thus, we have

$$
S_\alpha(\mathbf{x}, t) = \dot{S}_\alpha(\phi(\mathbf{x}, t)).
$$

Somewhat imprecisely, we refer to $\dot{S}_\alpha$ as the reaction rate of $\phi_\alpha$.

This set of equations (together with initial and boundary conditions) determines the velocity, composition and pressure fields provided that $S_\alpha$, $\tau_{ij}$ and $\bar{J}_\alpha$ are known.

Without doubt, a major achievement in combustion research in the last 20 years has been the accurate, detailed computations of laminar flames (e.g. Refs. 26–29). These computations entail the numerical solution of the conservation equations given above, with a detailed chemical kinetic scheme (to determine $S_\alpha$), and detailed modelling of molecular transport processes (to determine $\tau_{ij}$ and $\bar{J}_\alpha$). In these calculations typically of order 40 species are involved (i.e. $\sigma \approx 40$). The close agreement between these laminar-flame computations and experimental results clearly demonstrates—at least for simple fuels—that our knowledge of the chemical kinetics and molecular transport processes is sufficient for accurate calculations to be made from first principles.

Since turbulent combustion is governed by the same, known conservation equations, the question: can turbulent combustion be computed from first principles? reduces to a question of computational power. And, for the general case, the answer is simply: no. Neither now, nor in the foreseeable future, will computers have the power to provide accurate solutions to the full equations governing turbulent combustion.

For inert flows, direct numerical simulation (DNS), in which th Navier-Stokes equations (Eqs. 2 and 3) are solved, is an established research technique. It has provided extremely useful information about several geometrically-simple flows at
low or moderate Reynolds number. But for the higher Reynolds number flows in practical devices, informed estimates are that DNS is not feasible in the foreseeable future. 30

For two reasons, DNS of turbulent combustion is many orders of magnitude more demanding. First, the composition fields are likely to contain length scales and time scales smaller than those of the velocity field (i.e. the Kolmogorov scales). Second, the strongly-coupled set of $\sigma = 40$ composition equations with highly nonlinear source terms ($S_\alpha$) are much more difficult to solve than the Navier-Stokes equations. To illustrate this point, for a steady two-dimensional laminar methane flame, the computations performed by Smooke et al. required 150 hours of supercomputer time. 28

We conclude, then, that in the foreseeable future DNS is not feasible for turbulent combustion in practical devices, and consequently tractable alternatives must be sought.

(DNS is, however, a powerful research tool in the study of turbulent combustion. It has been applied directly to simulate simple turbulent flows involving simple reactions, 33-36 and also indirectly to study some of the fundamental processes involved in turbulent combustion. 37-40 Even with the simplest of flows and reactions, the direct approach is severely limited in the parameter range that can be studied.)

Moment Closures:

The simplest alternative approach is the mean-flow (or first-moment) closure, which is based on the conservation equations for the mean fields—the mean velocity field, $\langle \mathbf{U}(x,t) \rangle$, and the mean composition field $\langle \phi(x,t) \rangle$

As is now well recognized, an insuperable difficulty with this approach arises because of the highly nonlinear reaction rates. In order to solve the equation for $\langle \phi(x,t) \rangle$, the mean reaction rate $\langle S_\alpha(x,t) \rangle$ must be known, but the only straightforward approximation available

$$\langle S_\alpha(x,t) \rangle = \dot{S}_\alpha(\langle \phi(x,t) \rangle),$$

(c.f. Eq. 6) can be in error by several orders of magnitude.

The information needed to determine $\langle S_\alpha \rangle$ is provided by the joint probability density function (pdf) of the compositions, $f_\alpha(\psi_1, \psi_2, \ldots, \psi_\sigma, t)$, which is defined as follows. 32 Corresponding to each composition $\phi_\alpha$, we introduce an independent (sample-space) variable $\psi_\alpha$. Then $\psi = \{\psi_1, \psi_2, \ldots, \psi_\sigma\}$ can be viewed as a point in the $\sigma$-dimensional composition space. The joint pdf $f_\alpha(\psi_1, \psi_2, \ldots, \psi_\sigma, t)$ is, by definition, the probability density of the event $\phi(x,t) = \psi$. Alternatively it may be understood through the relation

$$f_\alpha(\psi_1, \psi_2, \ldots, \psi_\sigma, t) = \text{Prob}\{\psi_\alpha \leq \phi_\alpha(x,t) \leq \psi_\alpha + d\psi_\alpha\},$$

$$\leq \psi_\alpha + d\psi_\alpha,$$

$$\alpha = 1, 2, \ldots, \sigma,$$

where $d\psi = d\psi_1 d\psi_2 \ldots d\psi_\sigma$ denotes an infinitesimal hypervolume.

In terms of this joint pdf, the mean reaction rate is

$$\langle S_\alpha(x,t) \rangle = \int f_\alpha(\psi_1, \psi_2, \ldots, \psi_\sigma, t) \dot{S}_\alpha(\psi) d\psi,$$

where $d\psi$ indicates integration over the whole composition space.

There are two approaches to determining the joint pdf so that Eq. (9) can be used to determine the mean reaction rates. The first, discussed extensively below, is to solve a (modelled) conservation equation for $f_\alpha$ (or for another joint pdf): this is known as the pdf method.

In the second approach—the assumed pdf method—the joint pdf is assumed to have a particular form, which is parametrized by its first and second moments ($\phi_\alpha$ and $\phi_\alpha', \phi_\alpha''$) for which modelled conservation equations are solved. (See Refs. 36 and 41 for reviews.) (Here $\phi_\alpha'$ denotes the fluctuation $\phi_\alpha' = \phi_\alpha - \langle \phi_\alpha \rangle$.)

The assumed pdf method has proved successful for diffusion flames with simple chemistry. 13-16 As mentioned in the previous section, if chemical equilibrium is assumed, then all thermochemical properties are unique functions of the mixture fraction $\xi(x,t) = \phi_1(x,t)$. And consequently all thermochemical statistics can be determined from the pdf of $\xi$, $f_{\xi}$. There have been several suggestions for an assumed two-parameter form for $f_{\xi}$. These assumed forms can be regarded as satisfactory in that they generally have a similar shape to experimentally measured pdf's, and calculations based on them vary little among themselves. 14

Several diffusion-flame calculations have been made in which finite-rate chemistry has been incorporated through a reaction progress variable $c(x,t) = \phi_2(x,t)$. It is generally assumed that $c$ and $\xi$ are statistically independent, so that their joint pdf $f_{c\xi}$ is simply the product of their marginal pdf’s $f_c$ and $f_{\xi}$. And the assumed form of $f_c$ may be quite crude—the sum of three delta functions, for example.

The prospect is bleak for extending the assumed pdf method to more general cases. Consider, for example; applying the method to a methane/air diffusion flame, using a simplified four-step mechanism. This requires 5 composition variables (i.e. $\sigma = 5$). There are several major practical difficulties in implementing the method:

\begin{itemize}
  \item Possible values of $\phi$ are confined to an irregular region of the five-dimensional composition space.
  \item There is great difficulty in determining joint pdf's
\end{itemize}
confined to such regions with specified first and second moments.

ii) Modelled conservation equations have to be solved for the 5 first moments \( \langle \phi \rangle \), and for the 15 second moments \( \langle \phi \phi \rangle \). These 20 equations are strongly coupled, and the standard model equations are unlikely to guarantee realizability (i.e. the calculated moments may not correspond to a realizable joint pdf).

iii) The accurate numerical evaluation of 5-dimen-
sional integrals (e.g. Eq. 9) is far from trivial.

Beyond these formidable practical difficulties lies the unanswered question of whether the assumed joint pdf shape is accurate.

(Bockhorn\textsuperscript{44} reports an assumed pdf calculation involving some 12 compositions. The mean rates of two-body reactions are deduced from an assumed joint pdf of the two reactant concentrations and temperature.)

**PDF Methods:**

In discussing moment closures, our attention was confined to the closure problem associated with the nonlinear reaction rates, \( S_\phi(\phi) \). In pdf methods, this closure problem simply does not exist: in the exact conservation equation for \( f_\phi(\phi, z, t) \)—the composition joint pdf—the effects of reaction are in closed form\textsuperscript{35} (i.e. they do not need to be modelled).

Pdf methods are the subject of the next section. Here, we make just three observations.

i) As mentioned, the closure problem associated with \( S_\phi(\phi) \) is completely overcome.

ii) At first sight, pdf methods appear intractable because of the large dimensionality of the joint pdf's. But it is now well established that, through the use of Monte Carlo methods,\textsuperscript{36,25} the approach is quite tractable.

iii) In the context of turbulent combustion, the major closure problem in pdf methods is associated with molecular diffusion (i.e. the term \( \partial f_\phi / \partial x \) in Eq. 4). This problem is particularly difficult in (or near) the flamelet regime of turbulent combustion, where the small scales of the composition field \( \phi(z, t) \) are strongly influenced by reaction.

**Large-Eddy Simulations:**

For non-reactive flows, large-eddy simulations (LES)\textsuperscript{31,32,47} provide a tractable alternative to DNS. It is far from clear, however, that LES is a useful approach for turbulent combustion, because (unlike pdf methods) it does not overcome the closure problem associated with nonlinear reaction rates.

The starting point of the LES approach is to define resolved fields (e.g. \( U_\phi(z, t) \) and \( \phi_\alpha(z, t) \)) by the filtering operation:

\[
\phi_\alpha(z, t) = \int \phi_\alpha(y, t) G(|z - y|) dy,
\]

where integration is over all space, and, for definiteness, we consider the Gaussian filter

\[
G(s) = (\Delta \sqrt{2\pi})^{-3} \exp\left(-\frac{1}{2} \frac{s^2}{\Delta^2}\right).
\]

The specified filter width, \( \Delta \), corresponds to a length in the inertial subrange—much smaller than the integral length scale \( L \), but much larger than the Kolmogorov scale \( \eta \). Consequently the small-scale components of the fields \( U \) and \( \phi \) are contained in the residual or sub-grid scale fields \( \bar{U} \) and \( \bar{\phi} \):

\[
\phi_\alpha(z, t) = \phi_\alpha(z, t) - \bar{\phi}_\alpha(z, t).
\]

In LES for non-reacting flows, conservation equations are solved for the resolved fields. These equations contain terms of the form \( \bar{U}_i \bar{U}_j \) and \( \bar{U}_i \phi_\alpha \), which have contributions from both the resolved and residual fields. Sub-grid scale models are used to yield a closed set of equations by approximating \( \bar{U}_i \bar{U}_j \) etc. in terms of the resolved fields. While current sub-grid scale models may not be perfect, there are strong reasons to suppose that this approach should be successful: in view of the energy cascade, the statistics of the residual fields can be expected to be uniquely and universally related to the resolved fields.

For turbulent combustion the situation is quite different.\textsuperscript{36} The equation for the resolved composition \( \phi_\alpha(z, t) \) contains the filtered reaction rate \( S_\alpha(z, t) \). The problem of determining \( S_\alpha \) is precisely analogous to the problem of determining \( \langle S_\alpha \rangle \) in a mean-flow closure: the approximation

\[
\bar{S}_\alpha(z, t) = \langle \phi_\alpha(z, t) \rangle,
\]

can be in error by orders of magnitude. This is because of the nonlinearity of \( \bar{S}_\alpha \), and because \( \phi(z, t) \) varies significantly on sub-grid scales. The inapplicability of Eq. (13) is readily seen by considering combustion in the flamelet regime, with the flame thickness being much smaller than \( \Delta \). As observed by Givi,\textsuperscript{36} an appropriate evaluation of \( \bar{S}_\alpha \) has never been attempted in LES.

Not only is there a specific problem concerned with determining \( \bar{S}_\alpha \), but the general arguments to support sub-grid scale modelling break down. Again, this is most easily understood in the flamelet regime, in which reaction—which of course is a dominant effect—occurs on the smallest scales. And the small-scale structure of the composition field is dominated by the effects of reaction and diffusion, and are certainly not uniquely determined through a cascade process by the resolved fields.
At considerable cost, the closure problem associated with reaction rates in LES can be overcome by introducing a filtered density function \( F_\Phi(\psi; \xi, t) \) analogous to the composition joint pdf \( f_\Phi(\psi; \xi, t) \):

\[
F_\Phi(\psi; \xi, t) = \int \delta(\psi - \Phi(\xi, t)) G(|\xi - y|) dy. \tag{14}
\]

(Here \( \delta(\psi - \Phi) \) is written for the delta-function product \( \prod_{\alpha=1}^{\sigma} \delta(\psi_\alpha - \Phi_\alpha) \).) This has the interpretation that \( F_\Phi(\psi; \xi, t) \) is the fraction of the fluid around \( \xi \) (weighted by \( G \)) whose composition is in the infinitesimal range \( \psi_\alpha \leq \Phi_\alpha < \psi_\alpha + d\psi_\alpha, \alpha = 1, 2, \ldots, \sigma \).

Both in their definitions and properties \( f_\Phi \) and \( F_\Phi \) are very similar: they are related by

\[
f_\Phi = \lim_{\Delta \to 0} \langle F_\Phi \rangle. \tag{15}\]

In the conservation equation for \( F_\Phi \) (which is readily derived from Eqs. 4 and 14), the effects of reaction are in closed form, while the major closure problem is associated with molecular diffusion. In principle, a Monte Carlo method, similar to that used in pdf methods, can be used to solve the conservation equation for \( F_\Phi \).

We have introduced \( F_\Phi \), not to advocate its use, but to point out the limitations of using LES for turbulent combustion. Even using \( F_\Phi \), the same closure problem (associated with molecular diffusion) arises as in pdf methods. And the computational requirements are much greater since \( F_\Phi \) varies on the length scale \( \Delta \), while \( f_\Phi \) varies on the integral length scale, \( L \), and not at all in directions of statistical homogeneity.

PDF Methods

Pdf methods overcome the closure problem associated with nonlinear reaction rates. Their success, then, revolves around two issues. The first is the tractability of the numerical method to solve the modelled pdf equations, especially if realistic kinetics or complex flow-geometry is involved. The second is the accuracy of the modelling, especially that of molecular diffusion. In this section, some recent pdf calculations are shown to illustrate that substantial progress is being made on both issues. First, pdf methods are reviewed.

Methods Considered:

Turbulent combustion calculations have been performed using three different pdf methods, which are based, respectively, on: the joint pdf of composition \( f_\Phi(\psi; \xi, t) \); the joint pdf of velocity and composition \( f_{u\Phi}(\mathbf{V}; \psi; \xi, t) \); and, the joint pdf of velocity, dissipation and composition \( f(\mathbf{V}; \xi; \psi; \xi, t) \). Here \( \mathbf{V} = \{ \mathbf{V}_1, \mathbf{V}_2, \mathbf{V}_3 \} \) and \( \xi \) are the independent (sample-space) variables corresponding to velocity, and to the instantaneous mechanical dissipation \( \varepsilon(\xi, t) \).

While the composition joint pdf \( f_\Phi \) provides a complete one-point statistical description of the composition field, it contains no information about the velocity field. Consequently, in addition to the modelled equation for \( f_\Phi \), a turbulence model (e.g. \( k\varepsilon \) or Reynolds-stress) is needed to determine the mean-velocity and turbulence fields. In the transport equation for \( f_\Phi \), there is a term arising from the convective transport of compositions by the fluctuating velocity field \( \mathbf{u}(\xi, t) \) (where \( \mathbf{u} = \mathbf{U} - \langle \mathbf{U} \rangle \)). This is modelled as gradient-diffusion transport.

The velocity-composition joint pdf approach has the advantage that all forms of convective transport are treated exactly, since the corresponding term in the transport equation for \( f_{u\Phi} \) is in closed form. Consequently the assumption of gradient-diffusion transport is avoided. This approach has been successfully applied to premixed flames that exhibit counter-gradient diffusion, and to the early stages of development of a turbulent flame from a spark kernel. In this application, the gradient-diffusion assumption is significantly in error since the flame length scales are much smaller than the turbulence integral scale.

In addition, the use of the velocity-composition joint pdf \( f_{u\Phi} \) almost removes the need for a turbulence model. For, if \( f_{u\Phi} \) is known, so also are the mean-velocity and Reynolds-stress fields. But the joint pdf \( f_{u\Phi} \) contains no information about the length scales or time scales of turbulence. This information is needed because several modelled processes in the evolution of \( f_{u\Phi} \) proceed at the rate

\[
\Omega(\xi, t) = \langle \varepsilon(\xi, t)/k(\xi, t) \rangle. \tag{16}\]

Since the turbulent kinetic energy \( k \) is known from the joint pdf, \( \Omega(\xi, t) \) can be determined by solving the standard modelled dissipation equation \(^{12}\) for \( \langle \varepsilon(\xi, t) \rangle \).

In contrast to the two previous approaches discussed, that based on the joint pdf of velocity, dissipation and composition \( f(\mathbf{V}; \xi; \psi; \xi, t) \) provides a complete closure: the single modelled equation for \( f \) is closed. Hence the incompleteness of the velocity-composition joint pdf approach is remedied, and the need for the modelling equation for \( \langle \varepsilon \rangle \) is obviated. But more than this: the inclusion of \( \varepsilon \) within the pdf approach opens the way to more realistic modelling. Large fluctuations in the dissipation rate (i.e. internal intermittency) are ac-
counted for; and this information on the distribution of dissipation can be used in the modelling of molecular diffusion (and other processes).

(The time and length scale information contained in \( \int \Gamma \nu, \zeta, \psi_x, t \) pertains to the velocity field. It is inevitable, therefore, than any modelled equation for \( f \) contains the assumption that the scales of the composition fields are proportional to those of the velocity field. Means of including distinct scale information on the composition fields is discussed in the next section.)

**Lagrangian Viewpoint:**

The Lagrangian viewpoint is central to pdf methods because it poses modelling questions in a simple, natural way; and, similarly, it leads to an intuitively obvious solution algorithm. These points are illustrated here for a very simple case; and then, in the next sub-section, the general case is considered.

Consider the statistically-homogeneous field of a single reactive scalar \( \phi(\xi, t) \) in constant-density homogeneous turbulence. The conservation equation for \( \phi \) is

\[
\frac{D\phi}{Dt} = \Gamma \nabla^2 \phi + S,
\]  
(17)

which is Eq. (4) incorporating Fickian diffusion \( \rho_f \) = \(- \Gamma \nabla \phi \), with a constant diffusion coefficient, \( \Gamma \): Recall that \( \psi(\xi, t) \) is the reaction rate, which is a known function of the composition: \( \psi = \psi(\phi, t) \) (Eq. 6).

In view of the assumed statistical homogeneity, the composition pdf \( f_x(\psi; t) \) is independent of position. Its exact evolution equation is

\[
\frac{\partial f_x}{\partial t} = -\frac{\partial}{\partial \psi} \left[ f_x \left\{ (\Gamma \nabla^2 \phi) \psi + \dot{S}(\psi) \right\} \right],
\]  
(18)

where (for any function \( Q(\psi) \) \( \langle Q|\psi \rangle \) denotes the expectation of \( Q(\xi, t) \) conditional on the event \( \phi(\xi, t) = \psi \).

It may be seen from Eq. (18) that the reaction term is in closed form: for, if \( f_x \) is known, so also is \( \partial f_x / \partial \psi [f_x \dot{S}(\psi)] \). But the molecular diffusion term is not in closed form. And Eq. (18) presents the closure problem from the Eulerian viewpoint: it is required to model the conditional expectation \( \langle (\Gamma \nabla^2 \phi) \psi \rangle \) in terms of \( f_x(\psi) \).

The first and simplest closure approximation for molecular diffusion\(^{34,33,43}\) is

\[
\langle (\Gamma \nabla^2 \phi) \psi \rangle = -\frac{1}{2} C_\phi \Omega(\psi - \langle \phi \rangle),
\]  
(19)

where \( \Omega \) is the mean turbulence rate (Eq. 16), and the constant \( C_\phi \) is ascribed the value 2.0. A discussion of the physics of this model is deferred to the next section.

Substituting the model (Eq. 19) into the exact equation (Eq. 18) we obtain the modelled composition pdf equation

\[
\frac{\partial f_x}{\partial t} = -\frac{\partial}{\partial \psi} \left[ f_x \left\{ \frac{1}{2} C_\phi \Omega(\psi - \langle \phi \rangle) + \dot{S}(\psi) \right\} \right].
\]  
(20)

Given the turbulence rate \( \Omega(t) \) and the initial condition \( f_x(\psi; t_0) \), this equation can be solved to determine the subsequent evolution of the pdf.

We now introduce the Lagrangian viewpoint and show that the model, Eq. (19), has a simple interpretation.

Let \( x^*(t) \) denote the position of a fluid particle, i.e. a point that moves with the local fluid velocity; and let \( \phi^*(t) \) be the composition following the fluid particle:

\[
\phi^*(t) = \phi(x^*[t], t).
\]  
(21)

Then the evolution of \( \phi^* \) is given by (cf. Eq. 17)

\[
\frac{d\phi^*}{dt} = (\Gamma \nabla^2 \phi)^* + \dot{S}(\phi^*),
\]  
(22)

where the superscript \( \ast \) indicates that the quantity is evaluated at \( x^*(t) \).

The essence of the Lagrangian approach to modelling is to **model the rate of change of fluid-particle properties in terms of the particle properties themselves**. These models are usually stochastic, but here, for simplicity, we consider deterministic models.

It may be seen from Eq. (22) that the rate of change of \( \phi^* \) due to reaction is known in terms of \( \phi^* \), whereas the rate of change due to diffusion is not. It is intuitively clear that the deterministic particle model consistent with Eq. (19) is

\[
\frac{d\phi^*}{dt} = -\frac{1}{2} C_\phi \Omega(\phi^* - \langle \phi \rangle) + \dot{S}(\phi^*). \]  
(23)

(This is readily proved by the observation that the pdf equation derived from this particle model equation (Eq. 23) is identical to that stemming from Eq. 19, i.e. Eq. 20.) Thus, inspection of Eq. (23) reveals that a physical interpretation of the model (Eq. 19) is that molecular diffusion causes \( \phi^*(t) \) to relax to its mean value \( \langle \phi(t) \rangle \) at the rate \( 1/2 C_\phi \Omega \).

The following fundamental observations made from the above equations are true for the general case. For any process (e.g. reaction) that is completely
determined by the fluid-particle properties considered, the corresponding term in the pdf equation appears in closed form. Conversely, any process that is not known in terms of the fluid-particle properties (e.g., molecular diffusion) corresponds to a term in the pdf equation that has to be modelled.

The modelled equation for \( f_\phi(\psi; t) \) can readily be solved by several different numerical methods. But most of these methods are tractable when applied to joint pdf's of many variables (e.g. \( f(Y, z, \psi, x, t) \)). Monte Carlo methods, on the other hand, remain tractable and are now the accepted means of solving modelled pdf equations. The use of this method to solve Eq. (20) is now described.

The pdf \( f_\phi(\psi; t) \) is represented indirectly by a large number \( N (N = 10^2 - 10^3, \text{say}) \) of notional particles, the \( n \)-th having composition \( \phi^{(n)}(t) \). At the initial time \( t_0 \), the particle compositions are specified so that the distribution of \( \phi^{(n)}(t_0) \) is a good approximation to \( f_\phi(\psi; t_0) \). This can be done randomly—by choosing \( \phi^{(n)}(t) \) to be independent random numbers with distribution \( f_\phi(\psi; t_0) \)—or deterministically—by specifying \( \phi^{(n)}(t_0) \) such that

\[
F_\phi(\phi^{(n)}(t_0), t_0) = \left( n - \frac{1}{2} \right) / N, \quad (24)
\]

where \( F_\phi \) is the cumulative distribution function (cdf):

\[
F_\phi(\psi, t) = \int_\infty^{\psi} f_\phi(\psi^*; t) d\psi^*. \quad (25)
\]

Subsequently the particle compositions evolve according to Eq. (23).

From the particle properties, \( \phi^{(n)}(t) \), ensemble averages can be formed, which approximate means. For example the mean reaction rate \( \langle S(t) \rangle = \langle S(\phi(t)) \rangle \) is approximated by

\[
\langle S(t) \rangle_N = \frac{1}{N} \sum_{n=1}^{N} S(\phi^{(n)}(t)). \quad (26)
\]

It can be shown that this is a valid solution procedure, in that the ensemble averages obtained approximate the true means with an error that decreases (at least) as \( N^{-1/2} \).

For the present case of a deterministic model, the solution procedure described is simply the solution to the equation for \( F_\phi(\psi, t) \) (obtained by integrating Eq. (20)) by the method of characteristics. That is, \( F_\phi \) is conserved along the characteristics \( \phi^+(t) \).

It may be noted that, if Eq. (24) is used to specify the initial conditions \( \phi^{(n)}(t_0) \), the method involves no randomness, and therefore should not be referred to as a Monte Carlo method. In general, this type of method is better described as a particle method, since the essential ingredient is the indirect representation of the pdf by an ensemble of particles. It is this particle representation that makes the method tractable for joint pdf's of large dimension.

**Velocity-Dissipation-Composition Joint PDF:**

The ideas developed above are now applied to the joint pdf of velocity, dissipation and composition for a general, inhomogeneous, variable-density turbulent reactive flow.

A fluid particle has position \( \mathbf{x}^+(t) \), velocity \( \mathbf{U}^+(t) \), instantaneous dissipation rate \( \epsilon^+(t) \), and composition \( \phi^+(t) \). These Lagrangian variables are related to the Eulerian fields by, for example,

\[
\mathbf{U}^+(t) = \mathbf{U}(\mathbf{x}^+ - \mathbf{t}, t), \quad (27)
\]

cf. Eq. (21). And they evolve according to the exact equations (cf. Eqs. 3–4):

\[
\frac{d\mathbf{U}^+}{dt} = \mathbf{U}^+, \quad (28)
\]

\[
\frac{d\epsilon^+}{dt} = \mathbf{U}^+ \cdot \nabla \epsilon^+ + \frac{1}{\rho(\phi^+)} \left( \frac{\partial p}{\partial t} \right) \frac{\partial}{\partial \mathbf{x}^+} \left( \frac{1}{\rho(\phi^+)} \frac{\partial \mathbf{U}^+}{\partial \mathbf{x}^+} \right), \quad (29)
\]

\[
\frac{d\phi^+}{dt} = \dot{S}(\phi^+) - \frac{1}{\rho(\phi^+)} \frac{\partial \mathbf{U}^+}{\partial \mathbf{x}^+}, \quad (30)
\]

\[
\frac{d\epsilon^+}{dt} = \langle \dot{\epsilon} \rangle^+, \quad (31)
\]

The pressure has been decomposed into its mean \( \langle p \rangle \) and fluctuation \( p^\prime \); and a complicated expression for \( \dot{\epsilon} \) can be obtained from Eq. (3), but little is gained by doing so. The quantities in braces are not known in terms of the particle properties, and hence need to be modelled.

Equation (28), which is simply the definition of a fluid particle trajectory, appears trivial. But it has great significance: because the right-hand side is completely determined by particle properties, the process it represents—convective transport—is treated exactly in this pdf method. Thus gradient-diffusion assumptions are avoided.

In the velocity equation (Eq. 29), gravity and the mean pressure gradient are treated exactly, whereas the effects of the fluctuating pressure gradient and molecular stresses have to be modelled. In the composition equation (Eq. 30), the all-important reaction rate is known in terms of \( \phi^+ \), but molecular diffusion has to be modelled. There is no significant contribution to \( \dot{\epsilon} \) that can be expressed in terms of particle properties, and hence the whole process must be modelled.
The latest and best models for the terms in $\tau$, $p^*$, $J^*$ and $\dot{\epsilon}$ involve stochastic processes.\textsuperscript{23,52,53,55--58} For ease of understanding, we present here, instead, the earliest and simplest models.\textsuperscript{45,59,60} These are linear deterministic models analogous to that described in the previous sub-section (Eq. 23). With these models, the particle equations become

$$
\frac{dU_i^+}{dt} = g_i - \frac{1}{\rho(p_\Psi^+)} \frac{\partial (p)}{\partial x_i} - \frac{1}{2} \Omega H_y (U_j^+ - \bar{U}_j), \quad (32)
$$

$$
\frac{d\phi^+}{dt} = S_\phi (\phi^+) + \frac{C_4 \Omega (\phi^+ - \bar{\phi}_a)), \quad (33)
$$

$$
\frac{d\dot{\epsilon}}{dt} = \Omega \epsilon^+ (C_{31} P/\epsilon - C_{43}) - C_{45} \Omega (\epsilon^+ - \bar{\epsilon}), \quad (34)
$$

where a tilde denotes the density-weighted mean (e.g., $\bar{\phi}_a = \langle \rho \phi_a \rangle / \langle \rho \rangle$). Further, $\dot{u}_i^+ \dot{u}_j^+$ is the density-weighted Reynolds stress, $\bar{k} = 1/2 \dot{u}_i^+ \dot{u}_j^+$ is the kinetic energy, and we redefine $\Omega$ as $\bar{\epsilon}/k$.

The composition equation (Eq. 33) is essentially the same as before: in addition to changing with the reaction rate, $\phi^+$ tends to relax to $\phi$ at the rate $1/2C_4 \Omega$.

In the velocity equation (Eq. 32), $H_y$ is a non-dimensional tensor function of Reynolds stresses, mean velocity gradients and $\Omega$. The kinetic energy balance imposes the constraint

$$
H_y \dot{u}_i^+ \dot{u}_j^+ = 2 \bar{k}, \quad (35)
$$

from which it follows than in isotropic turbulence $H_y$ is simply $\bar{\delta}_y$. Thus in isotropic turbulence the modelled term tends to make $U_i^+$ relax to $\bar{U}_i$ at the rate $1/2 \Omega$.

In general, $H_y = \delta_y$ provides a poor model since it yields no return to isotropy for the Reynolds stresses. The simplest model without this defect (and consistent with Eq. 35) is

$$
H_y = \delta_y + C_H \left( \frac{\dot{u}_i^+ \dot{u}_j^+}{\bar{k}} - \frac{1}{2} \bar{S}_{ij} \dot{u}_i^+ \dot{u}_j^+ / \bar{k}^2 \right), \quad (36)
$$

which, with $C_H = 10.0$, yields reasonable levels of anisotropy in homogeneous shear flow. Better models can, of course, be constructed; in fact, there is a choice of $H_y$ corresponding to every (realizable) Reynolds-stress model.

In the dissipation equation (Eq. 34), $P$ is the production rate of $\bar{k}$, and $C_{31}$ and $C_{43}$ are standard model constants.\textsuperscript{11,12} The term involving these quantities causes the mean $\bar{\epsilon}$ to evolve according to the standard model equation, while the final term tends to make $\bar{\epsilon}^*$ relax to the mean $\bar{\epsilon}$ at the rate $C_{43} \Omega$, where $C_{43}$ is a positive constant.\textsuperscript{60}

Our purpose here is just to illustrate the method. Consequently the many shortcomings of these linear deterministic models are not discussed: the better models currently in use are described in the references.

For variable-density flows it is most convenient to consider the mass density function $F(\nabla, \zeta, \Psi; \bar{\xi}, \bar{\eta})$, which is simply the joint pdf $f(\nabla, \zeta, \Psi; \bar{\xi}, \bar{\eta})$ multiplied by the density $\rho(\Psi)$. Corresponding to the particle equations (Eqs. 28, 32--34), the closed model equation for $F$ is

$$
\frac{\partial F}{\partial t} + V_i \frac{\partial F}{\partial x_i} + \frac{\partial}{\partial \bar{\xi}} \left( F \left( \frac{g_i - 1}{\rho(\Psi)} \frac{\partial (p)}{\partial x_i} - \frac{1}{2} \Omega H_y [V_j - \bar{U}_j] \right) \right) + \frac{\partial}{\partial \bar{\eta}} \left( F \left( \frac{S_\phi (\Psi)}{1} C_4 \Omega (\phi^+ - \bar{\phi}_a) \right) \right) + \frac{\partial}{\partial \bar{\xi}} \left( F (\Omega \zeta (C_{31} P/\bar{\epsilon} - C_{43}) - C_{45} \Omega (\zeta - \bar{\epsilon})) \right) = 0. \quad (37)
$$

All the coefficients in this equation (e.g. $\bar{U}_i$, $\bar{\epsilon}$, $\Omega$) can be determined from $F$ by, for example,

$$
\bar{\epsilon} = \int \zeta F \, d\bar{\xi} d\bar{\eta} (d\bar{\eta} / \rho). \quad (38)
$$

(The mean pressure gradient is also determined by $F$, but not in such a straightforward way.\textsuperscript{29})

The particle method\textsuperscript{25} used to solve Eq. (37) for $F$ is more complicated than that described in the previous subsection, because of the assumed inhomogeneity and variable density. It is, however, a very natural approach.

At time $t$, let $M(t)$ be the mass of fluid in the solution domain. The state of the fluid (or alternatively, $F$) is represented by a large number $N(t)$ of notional particles, each of the same fixed mass $m \langle N(t) = M(t)/m \rangle$. The $n$-th particle has position $\bar{z}^{(n)}(t)$, velocity $\bar{U}^{(n)}(t)$, dissipation $\bar{\epsilon}^{(n)}(t)$ and composition $\phi^{(n)}(t)$; these properties evolve in time according to the particle equations (Eqs. 28, 32--34). In principle, means can be determined as follows. Consider a cell of volume $\Delta x^3$ centered at position $\bar{z}_i$ and let $K(\bar{z}, t)$ be the number of particles within the cell. Then the mean fluid density is

$$
\langle \rho(\bar{z}, t) \rangle = mK(\bar{z}, t)/\Delta x^3. \quad (39)
$$

Other density-weighted means are approximated by ensemble averages, e.g.

$$
\bar{\epsilon}(\bar{z}, t) = \frac{1}{K(\bar{z}, t)} \sum_{K(\bar{z}, t)} \bar{\epsilon}^{(n)}(t), \quad (40)
$$
where the summation is over all particles in the cell. The statistical error in these approximations is proportional to $N^{-1/2}$. (In practice a more sophisticated method of extracting means is used that reduces the error—although it remains of order $N^{-1/2}$.)

Inflow and outflow boundaries are treated in an obvious way, by adding and removing particles. At walls, specular reflection is used, but these conditions have not been studied in detail.

In summary: the single modelled equation for the joint pdf (or mass density function) Eq. (37) provides a closure for turbulent combustion. This equation can be solved by a particle method, the essence of which is to solve a coupled set of ordinary differential equations (Eqs. 25, 32–34) for a large number of particles. Closure is achieved by modelling the behavior of fluid-particle properties: convection and reaction are treated exactly. The practicability of this type of approach has been established through application to a variety of turbulent combustion problems (reviewed below).

Implementation of Reaction:

PDF methods are described above for a general set of $\sigma$ compositions $\phi = \{\phi_1, \phi_2, \ldots, \phi_{\sigma}\}$. In detailed computations of laminar flames, typically 40 compositions are required. Is it computationally feasible to solve the joint pdf equation with $\sigma = 40$?

It is quite feasible to use the particle method to solve the modelled equation for the joint pdf of 40 non-reactive compositions. The storage requirement $N\sigma \approx 4 \times 10^6$ (for $N = 10^5$, $\sigma = 40$) is not prohibitive. And, with $S = 0$, the particle equation (Eq. 33) is trivial to integrate.

For 40 reactive compositions, the storage requirement is the same, but the difficulty of integrating the particle equations increases enormously. Equation (33) is a set of 40 stiff ordinary differential equations which is to be solved about $10^7$ times (once for each of $10^5$ particles on each of 100 time steps, say). Based on the performance of current chemical kinetics codes, it can be estimated that each such integration requires at least $1/10$ s of supercomputer time. Thus the total time required is $10^8 s \approx 280$ hrs. We conclude, then, that this direct approach of using detailed kinetics will not be feasible for some time.

The alternative approach adopted by all researchers is to use a reduced kinetic scheme (involving 5 or fewer compositions), and to employ a table-look-up procedure to integrate the composition equation (Eq. 33). For example, Chen et al. describe the implementation of a four-step (five-composition) mechanism for methane combustion. Using this mechanism, tables are created of the change in composition due to reaction $\Delta \phi$ over specified time intervals $\Delta t$, as a function of the initial composition $\phi$. These tables are then used to integrate the particle equations very efficiently. The principal computational consideration with this approach is storage, since several $\sigma$-dimensional tables are required.

Both the formulation of reduced mechanisms and the table-look-up procedures appear to be in an early stage of development, requiring significant insight and labor on the part of the researcher. There is no inherent reason why this task cannot be automated. A challenge for the future is to develop a computational procedure that, given a detailed mechanism, will generate an optimum reduced mechanism and table-look-up procedure. Some progress in this direction is reported by Chen and by Maas & Pope.

Applications:

We briefly review here previously-reported pdf calculations (based on particle methods) of turbulent combustion involving finite-rate kinetics.

For premixed combustion, Pope solved the equation for the joint pdf of three compositions to calculate the oxidation of CO and the formation of NO in a propane-air flame stabilized behind a perforated plate. Other premixed-flame calculations have been performed that demonstrate different attributes of pdf methods, but not with finite-rate kinetics.

Most premixed flames are in the flamelet regime, in which reaction and molecular diffusion are strongly coupled. Current mixing models do not incorporate this coupling realistically (if at all). This has led to alternative closure strategies based on flamelet approaches. These issues form the subject of the next section.

Many more calculations have been reported of turbulent diffusion flames. Pope & Corredes made calculations of a CO/H$_2$/N$_2$-air diffusion flame, using the joint pdf of velocity and two compositions. The calculated mean profiles at 25 nozzle diameters are shown on Fig. 1, and the rms OH profile at the same location is shown on Fig. 2. The reaction scheme employed assumes that the reaction CO + OH $\rightarrow$ CO$_2$ + H is in partial equilibrium. This assumption breaks down in the center of the flame (where the temperature is low) which accounts for the observed difference between the calculated and measured CO and OH profiles in this region. Apart from these discrepancies, the calculations are in excellent agreement with the data. With 35,000 particles and 650 steps, these computations required 65 CPU minutes on an IBM 3084.

The good agreement between the pdf calculations and the measurements shown on Figs. 1 and 2 cannot, however, be taken as firm evidence for the validity of the assumptions on which the cal-
trated below, measurements of more detailed statistics are needed in order to discriminate between these models.

Both Jones & Kollmann and Chen & Kollmann report calculations based on the joint pdf of three or four compositions for the propane/air jet diffusion flames measured by Godoy. The general conclusion is that the reduced reaction mechanisms used are inadequate. Similar calculations for H2-air diffusion flames are reported by Chen & Kollmann and Barlow et al.

Our understanding of finite-rate-chemistry effects in turbulent flames has been greatly advanced by application of laser diagnostics to the carefully-conceived piloted jet diffusion flame of Masri & Bilger. Detailed measurements of these flames have been reported—including joint pdf’s or scatter plots of major and minor species—with methane, propane and a CO/H2/N2 mixture as the fuel. Non-equilibrium effects are clearly evident, including local extinction in the CH4 flames.

Chen and coworkers have performed several pdf studies of these flames, the calculations being based on the joint pdf of 4 or 5 compositions and a Reynolds-stress closure. For the methane flames, different reduced schemes have been employed including 4-step schemes (requiring 5 compositions); and for the CO/H2/N2 flames a 3-step scheme is used.

Figure 3 (from Chen & Dibble) shows scatter plots of fuel and oxygen mass fractions at 20 nozzle diameters for two methane-air flames. In flame B there is substantial local extinction, whereas in flame L (which has a lower jet velocity) there is not. Even for flame L the experimental data show significant co-existence of fuel and oxygen, much more than in strained laminar flames (shown as lines). For flame B, the experimental points appear to congregate in a band, with significantly greater co-existence of CH4 and O2 than in flame L. The pdf computations show, at least qualitatively, the same behavior. (In the calculations, two different four-step schemes were used: one due to Bilger, the other to Peters & Sheshadri (denoted by P&S). Details are given in Ref. 86.)

There are, however, significant differences between the pdf computations and the experimental data. For example, Fig. 4 (from Chen & Dibble) shows scatter plots of CO and mixture fraction for the same methane-air flames. Chen & Dibble suggest that experimental errors are responsible for some of the high CO points; but they also suggest that the discrepancy is due in part to the inadequacy of current mixing models.

To illustrate a different point, we show on Fig. 5 (from Chen, Bilger & Dibble) scattering plots of H2O mass fraction and mixture fraction obtained for the CO/H2/N2-air flame. For given mixture fraction, the experimental points show a broad distri-
Fig. 3. Scatter plots of CH₄ and O₂ mass fractions in a piloted methane-air diffusion flame. Upper four figures: composition joint pdf calculations using two different 4-step kinetic schemes. Lower two figures: experimental data. Flame B is closer to extinction than flame L. The four lines (in order of increasing Y₀₂) are for: laminar flame, strain-rate \( a = 100 \text{ s}^{-1} \); \( a = 300 \text{ s}^{-1} \); \( a = 450 \text{ s}^{-1} \); and, inert mixing. (From Ref. 86).
Fig. 4. Scatter plots of mass fraction of CO and mixture fraction for the same conditions as Fig. 3. The three lines (in order of increasing $Y_{\text{CO}}$) are: strained laminar flame, $a = 100$ s$^{-1}$; $a = 300$ s$^{-1}$ (barely distinguishable); and $a = 450$ s$^{-1}$. (From Ref. 86).

bution centered, approximately, on the laminar-flame value. Clearly, the scatter plot obtained from the pdf calculations is qualitatively incorrect. In the pdf model, no allowance is made for differential diffusion—that is, for the different molecular diffusion rates of the different species. As a consequence, the points on the scatter plot inevitably fall inside the indicated triangle. Both the experimental points and the laminar-flame lines lie partly outside this triangle, thus providing direct evidence of the effects
of significant differential diffusion—effects first reported by Drake et al.\textsuperscript{88,89}

Calculations of the piloted methane-air flame have been performed by Masri & Pope,\textsuperscript{90} using the joint pdf of velocity and mixture fraction. At present, Masri, Norris & Pope are performing calculations of the same flames using the joint pdf of velocity, dissipation and five compositions, incorporating a 4-step scheme.

Though their thermochemistry is complex, the flow geometry of jet diffusion flames is simple. The flames are statistically axisymmetric, and the Monte Carlo method can be implemented as a marching procedure (marching in the axial direction) because the boundary-layer approximations can be invoked.\textsuperscript{25} We now cite two examples of the application of the velocity-composition pdf method to more complex flows.

Anand et al.\textsuperscript{91,92} report calculations of two-dimensional non-reacting recirculating flows, using two different algorithms. In the first,\textsuperscript{91} the Monte Carlo method is coupled to a standard finite-volume code which is used, primarily, to determine the mean pressure field. In the second algorithm,\textsuperscript{92} a Poisson equation is solved for the mean pressure, thus removing the need for a finite-volume code. Haworth & El Tahry,\textsuperscript{93,94} have developed a coupled Monte Carlo/finite volume algorithm (similar to that of Anand et al.\textsuperscript{91}) to solve the pdf equation for the transient two- and three-dimensional flow within the cylinder of spark-ignition engines.

From this brief survey of recent applications we draw three conclusions:

i) It has been amply demonstrated that pdf methods are computationally tractable even with complex flow geometry and with realistic (i.e. 4-step) reaction schemes. (However, considerable effort could profitably be expended to improve the existing algorithms in many respects.)

ii) The scatter plots demonstrate that both measurement techniques and pdf methods have developed to the stage that issues related to finite-rate kinetics can be addressed.

iii) The principal weakness in the current models is the treatment of molecular diffusion. Models are needed that account for the effects of reaction on diffusion and, perhaps, also that account for differential diffusion.

Coupled Reaction and Diffusion

As concluded above, the principal weakness in the current models is the treatment of molecular diffusion. In this context we now discuss the current problems and promising future directions.

In a very simplistic view, the coupling between
reaction and diffusion is parametrized by the Damkohler number defined by
\[ Da = \frac{\tau_\eta}{\tau_c}, \]  
(41)

where \( \tau_\eta \) is the Kolmogorov time scale and \( \tau_c \) is the characteristic chemical time scale. In the next two subsections the idealized extreme cases \( Da \ll 1 \) (distributed combustion) and \( Da \gg 1 \) (flamelet combustion) are considered. Then the more realistic practical situation is discussed.

**Distributed Combustion:**

In turbulence, molecular diffusion is associated predominantly with the smallest scales of the composition fields, since these contain the steepest gradients. In the absence of reaction, there is a dynamic equilibrium between the turbulent folding and straining of the fluid that intensifies the composition gradients, and molecular diffusion which reduces them. The characteristic time scale of this dynamic process is \( \tau_\eta \). In the presence of reaction with \( Da \ll 1 \), reaction occurs too slowly for it to affect these processes significantly. Hence for this case of distributed combustion (\( Da \ll 1 \)) there is essentially no coupling between reaction and diffusion. And a model for molecular diffusion that successfully describes the mixing of inert species is equally applicable to distributed combustion.

In most pdf calculations of inert mixing or distributed combustion, molecular mixing is treated by stochastic mixing models. These models,\(^{56,95,96}\) also referred to as particle-interaction models, can be viewed as extensions of Curl's coalescence/dispersal model.\(^{97}\) They have three favorable properties:

1. they are applicable to an arbitrary number of compositions;
2. they satisfy the appropriate linearity and independence principles;\(^{96}\)
3. they automatically guarantee realizability, in particular the boundedness of compositions.

On the other hand, they lack the following attributes:

4. qualitative and quantitative accuracy for the simplest test case of a decaying composition field in isotropic turbulence;\(^{96}\)
5. a sound physical, mathematical or empirical basis;
6. the treatment of Reynolds-number or Schmidt-number effects, including differential diffusion; and
7. correspondence to a realistic model for the time series of composition \( \psi(t) \) following a fluid particle.

Recent work relating to these models is contained in Refs. 57, 58, 99–102.

To illustrate item (4), Fig. 6 shows the evolution of the pdf of a single conserved scalar according to a stochastic mixing model\(^{96}\) (Fig. 6b), and the true result obtained from direct numerical simulations\(^{103}\) (DNS) (Fig. 6a). It may be seen that at early times the stochastic model generates a pdf with a distinctly flat central portion, rather than the concave shape obtained from DNS. At large times the shapes appear similar, but the flatness factor of the modelled pdf tends to infinity, rather than to the Gaussian value of 3.

Recently Kraichnan and coworkers\(^{104–107}\) have developed a radically new formalism to produce pdf closures, referred to as mapping closures. When applied to the test case mentioned above (see Fig. 6c), the agreement with the DNS data is striking: and the modelled pdf tends, correctly, to a Gaussian for large times. This new mapping closure, then, possesses attributes 3–5: further development of the methodology is required to determine whether it possesses the other attributes.

**Flamelet Combustion:**

By the definition used here, in flamelet combustion, reaction takes place (almost exclusively) in

---

**Fig. 6.** Evolution of the pdf of an inert passive scalar in isotropic turbulence: a) from DNS,\(^{103}\) b) stochastic mixing model,\(^{96}\) c) Kraichnan’s model.\(^{104–107}\) The value of the pdf at the origin increases with time.
thin sheets that locally have the same structure as steady, plane, strained laminar flames. In this definition—which applies both to premixed and diffusion flames—the phrase "almost exclusively" is needed in view of the occurrence of cusps and critical points: but the definition deliberately excludes the occurrence of local extinction. A necessary (but not sufficient\(^1\)) condition for flamelet combustion is \(\text{Da} \gg 1\).

This regime is inherently difficult to treat in a traditional one-point closure. For the small-scale structure of the composition field is dominated by reaction (strongly coupled with diffusion) rather than being determined by the large scales via a cascade process. Instead, flamelet models\(^2\) that explicitly represent the flame-sheet structure offer a more natural approach.

For turbulent diffusion flames, the flamelet model\(^106-110\) relates the local composition \(\Phi\) to the local mixture fraction \(\xi\) and its dissipation rate \(\chi\). Hence, the joint pdf of \(\Phi\) is known in terms of the joint pdf of \(\xi\) and \(\chi\). Calculations based on the flamelet model have been performed both using moment closures\(^109,111\) and pdf methods.\(^71,72,90\) The analysis of Peters\(^110\) establishes a sound theoretical basis for the flamelet model, and there is little doubt that this is the method of choice, when it is applicable.

For premixed turbulent flames, flamelet concepts have been premixed in some time for closure models both for moment closures (e.g. the Bray-Moss-Libby model\(^112\)) and for pdf methods.\(^68\) Recently, several new models that represent flamelet statistics explicitly have been proposed,\(^69,113-117\) drawing on the earlier work of Marble and Broadwell.\(^118\) In these models, the primary dependent variable is the expected surface-to-volume ratio (or area density) \(\Sigma(x,t)\) of the flame sheet (or an equivalent quantity). In general, turbulent straining tends to increase \(\Sigma\), while the combination of flame propagation and curvature tends to decrease \(\Sigma\). Both these processes have to be modelled, and the modelling is at an early stage of development, with major differences between the different proposals.

**General Case:**

It should be recognized that the two cases discussed above (\(\text{Da} \ll 1\) and \(\text{Da} \gg 1\)) are idealizations. In practice, in a given turbulent combusting flow, there is a large range of chemical time scales (\(\tau_c\)) and a large range of turbulent time scales (\(\tau_t\)). To illustrate the range of chemical time scales, Correa\(^119\) performed detailed kinetic calculations for a methane-air mixture at conditions typical of a lean premixed gas-turbine combustor. For four elementary reactions the corresponding time scales were found to be:

\[
H + O_2 \Leftrightarrow OH + O, \quad \tau_c = 2 \times 10^{-7} \text{ s}, \quad \text{(RI)}
\]

\[
CO + OH \Leftrightarrow CO_2 + H, \quad \tau_c = 2 \times 10^{-5} \text{ s}, \quad \text{(RII)}
\]

\[
H + OH + M \Leftrightarrow H_2O + M, \quad \tau_c = 7 \times 10^{-5} \text{ s}, \quad \text{(RHI)}
\]

\[
N_2 + O \Leftrightarrow NO + N, \quad \tau_c = 4 \times 10^{-2} \text{ s}. \quad \text{(RIV)}
\]

Thus the chain-branching reaction (I) is two orders of magnitude faster than reactions II and III, while the NO production reaction is slower (than II and III) by three orders of magnitude.

A characteristic local turbulent time scale (\(\tau_t\)) can be defined in terms of the local scalar dissipation

\[
\tau_t = \chi^{-1}, \quad \chi = \nabla \xi \cdot \nabla \xi, \quad \text{(42)}
\]

or in terms of the local velocity gradients

\[
\tau_a = a^{-1}, \quad a^2 = \frac{\partial u_i \partial u_i}{\partial x_j \partial x_j}. \quad \text{(43)}
\]

(\(\chi\) may be noted that the Kolmogorov scale is \(\tau_\kappa = \left(\frac{\chi}{\kappa^2}\right)^{-1/2}\).) The range of time scales can be estimated from the known distributions of \(a\) or \(\chi\)—we use the latter.

To a good approximation \(\chi\) is log-normally distributed\(^103,120,121\) and hence so also is \(\tau_c\). The variance \(\sigma^2\) of \(\ln \chi\) increases weakly with Reynolds number. Dowling’s measurements\(^120\) in axisymmetric jets with nozzle-Reynolds numbers of 5,000 and 16,000 support a value \(\sigma^2 \approx 5\). Let \(\tau_{0.8}\) and \(\tau_{0.2}\) be relatively large and small times such that each of the events \(\tau_c > \tau_{0.8}\) and \(\tau_c < \tau_{0.2}\) has probability 0.2. Then, from the given distribution of \(\chi\), the time-scale ratio \(\tau_{0.8}/\tau_{0.2}\) is deduced to be 300.

We conclude, then, that in a given turbulent combusting flow, the Damköhler number \(\text{Da} = \tau_c/\tau_t\) can differ by 4 orders of magnitude, depending on which reaction time scale \(\tau_c\) is used, and whether \(\tau_{0.8}, \tau_{0.2}\) or \(\tau_n\) is taken for the turbulent time scale \(\tau_t\). A model that attempts to treat the interaction between reaction and diffusion, and that makes either of the extreme assumptions \(\text{Da} \gg 1\) or \(\text{Da} \ll 1\), cannot therefore be expected to have a significant range of applicability.

As stated in the previous sub-section, for the extreme case \(\text{Da} \gg 1\), flamelet models are soundly based, and are generally the method of choice. But for flames involving local extinction, an appropriately defined Damköhler number is inevitably of order unity or less. For this case, the assumptions on which the simple flamelet model are based are invalid; and the additional assumptions made to account for extinction, partial premixing, and re-ignition lack the sound foundations of the basic high-Damköhler-number theory. Further, the growing body of detailed experimental data\(^6-8\) on the local composition in turbulent flames provides strong *prima facie* evidence that combustion in these flames does not occur in flamelets (see e.g. Fig. 3).
Improved Modelling:

The preceding considerations lead to the conclusion that what is needed is a general model (not restricted to simple premixed or diffusion flames) that is applicable to all Damkohler numbers—one that accounts for the effects of flamelet structure at high Damkohler number, without imposing this structure explicitly by assumption. How is this to be achieved?

While they may not provide a complete solution, the current stochastic models can be improved in several respects. Only recently have pdf methods (incorporating stochastic mixing models) been examined in detail in applications with finite-rate kinetics.58,101 These studies have revealed and remedied some glaring deficiencies of the models, but much more can be done. At present the models contain the single turbulent time scale $k/\langle \epsilon \rangle$, and reaction and diffusion do not occur simultaneously at finite rates. There is no difficulty in incorporating a range of time scales$^{41}$—through the stochastic model$^{102}$ for $\epsilon^+(t)$, for example—and allowing reaction and mixing to occur simultaneously. In this way the temporal structure of the composition fields can be simulated realistically.

But at this level of closure (i.e. the joint pdf of $U$, $\epsilon$ and $\phi$), the small-scale spatial structure of the composition fields is not represented. Of the several possible ways that this structure can be (partially) represented, the most promising appears to be through the joint pdf of $U$, $\epsilon$, $\phi$ and $\nabla \phi$: that is, to incorporate the composition gradients within the pdf method. For a single scalar $\phi(\gamma)$, if the field is isotropic (or locally isotropic) no information is lost if, instead of $\gamma(\gamma) = \nabla \phi$, one considers the statistics of $\gamma(\gamma) = |\nabla \phi|$ or, equivalently, those of the scalar dissipation $\chi = \Gamma \gamma^2$. The modelling of the evolution equation for the joint pdf of $\phi$ and $\gamma$ has previously been considered by Meyers & O'Brien$^{122}$ and by Kraichnan and coworkers$^{104,105}$. The further development of mapping closures for this joint pdf holds great promise.

From the Lagrangian viewpoint, the addition of $\nabla \phi$ within the pdf method requires the development of a stochastic model for $\nabla \phi^+(t)$—that is, a model for $\nabla \phi$ following a fluid particle. In the exact equation for the evolution of $\nabla \phi^+(t)$, the effects of reaction appear in closed form, while the effects of straining and diffusion require modelling. (A successful model for the velocity gradients $\partial u_i/\partial x_j$ has already been developed$^{123}$.)

The additional information provided by $\nabla \phi$ is most likely sufficient to remove the current dichotomy between flamelet and non-flamelet models. This is most clearly seen for diffusion flames. Both in the simple flamelet model$^{110}$ and in the perturbation analysis$^{124}$ of diffusion flames, a central role is played by the joint pdf of $\xi$ and $\chi$: the joint pdf of $\phi$ and $\nabla \phi$ contains the same information.

In flamelet models of premixed combustion, the primary statistic is the surface-to-volume ratio $\Sigma(\gamma, t)$. The surface in question (i.e. the flame sheet) is usually defined as a propagating surface, but it can equally well be defined as a constant-property surface. For example, with $\phi(\gamma, t)$ being the reaction progress variable (often denoted by $c$) Cant et al.$^{113}$ define the flame sheet to be the constant-property surface on which $\phi(\gamma, t) = \phi^*$ (where $\phi^*$ is specified to be the value of $\phi$ at the inflexion point of the laminar flame profile). There is a mathematical relationship between $\Sigma(\gamma, t)$ and the joint pdf $f_{\phi \gamma}$ of $\phi(\gamma, t)$ and $\gamma(\gamma, t) = |\nabla \phi|$, first stated by Bilger$^{126}$ and established rigorously in the Appendix: it is

$$\Sigma(\gamma, t) = \int_0^\infty \eta f_{\phi \gamma}(\phi^*, \eta; \gamma, t) d\eta = f_{\phi}(\phi^*, \gamma, t)(\gamma | \phi = \phi^*), \quad (44)$$

where $f_{\phi}$ is the pdf of $\phi$. Thus the joint pdf of composition and its gradient also contains information about the surface-to-volume ratio.

It appears feasible, then, to develop a tractable pdf method incorporating the composition gradients that is generally applicable and that reduces, correctly, to flamelet models in the appropriate extreme limiting cases. At this level of closure, it should be possible to incorporate the effects of Reynolds number and Schmidt number (including differential diffusion). The development of such a model will be greatly aided by DNS and experimental techniques$^{127}$ that are capable of resolving the fine-scale composition fields.

Conclusion

The central question that has been addressed is: how can realistic finite-rate kinetics be incorporated.
in turbulent combustion models for practical devices? For generations to come, this will not be achieved by DNS. And the appeal that LES has for inert flows vanishes for turbulent combustion, because it does not overcome the major closure problem caused by non-linear reaction rates.

It is now well established that pdf methods are tractable for complex flows and with realistic finite-rate kinetics. In the method based on (at least) the joint pdf of velocity and composition, both reaction and convective transport are treated exactly, without modelling assumptions. This clearly provides a more accurate closure than the assumed-pdf method, since no assumption about pdf shape is made. Further, the assumed-pdf method runs into several practical difficulties when more than one or two compositions are required.

At present, the weakest component of pdf methods is the modelling of molecular diffusion, especially in the presence of reaction. For diffusion flames in the extreme flamelet limit (Da ≫ 1), flamelet models treat the coupling between reaction and diffusion accurately and elegantly. But, it is argued, flamelet models have quite limited applicability since, in practice Da spans, typically, four orders of magnitude.

The stochastic mixing models currently used in pdf methods to model molecular diffusion can be improved in several respects. In particular, a range of turbulent time scales can be incorporated, and reaction and diffusion can be treated simultaneously. These improvements can lead to a realistic representation of the temporal structure of the composition fields; but this level of closure contains no information on the small-scale spatial structure. Such information can be incorporated by extending the pdf considered to include the composition gradients. An attraction of this level of closure is that flamelet and non-flamelet concepts can be reconciled for premixed, diffusion and more general flames. For the joint pdf of composition and its gradients contains the information used in flamelet models—specifically, the scalar dissipation and the surface-to-volume ratio.

In conclusion we observe that the conditions are ripe for further significant progress. The methodology of laminar flame calculation is well developed, and can be used to address questions on reduced kinetics schemes, the importance of differential diffusion, and the nature of extinction and ignition. Direct numerical simulations (and, to a lesser extent, laser diagnostics) can be used to investigate small-scale processes in simple reactive flows. Mapping closures can be developed for the joint pdf of composition and its gradient. And, most importantly, laser diagnostics will continue to provide essential detailed information on the distribution of compositions in turbulent flames.

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REFERENCES

109. LIEW, S. K., BRAY, K. N. C. AND MOSS, J. B.:
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Appendix

With $\phi(x)$ being a differentiable scalar field (e.g. mixture fraction), we consider the constant-property surface $S(\psi)$ consisting of the points $x$ that satisfy $\phi(x) = \psi$. Expressions are derived here relating statistics of $S(\psi)$—e.g. its surface to volume ratio $\Sigma(x, \psi)$—to statistics of $\phi(x)$ and its gradient $\gamma(x) = |\nabla \phi|$.

This is achieved by obtaining two independent expressions for the quantity $G(\eta, \psi, d\psi)$, now defined. Let $I(\psi, \eta, d\psi)$ be the indicator function for the event $\psi < \phi(x) < \psi + d\psi$ (see Fig. 7). That is, $I = 1$ when the event occurs and zero otherwise. With $\Omega$ being an arbitrarily chosen volume in physical space, $G$ is defined by

$$G(\eta, \psi, d\psi) = \left( \int_{\Omega} I(\psi, \eta, d\psi) \delta(\eta - \gamma(x)) d\psi \right). \quad (A1)$$

Let $f(\psi, \eta, z)$ (denoted by $f_{\phi, \eta}$ in the text) be the joint pdf of $\phi(x)$ and $\gamma(x) = |\nabla \phi|$, where $\eta$ is a sample-space variable corresponding to $\gamma$. This can be expressed as

$$f(\psi, \eta, z) = (\delta(\psi - \phi(x)) \delta(\eta - \gamma(x))). \quad (A2)$$

Now, since the indicator function can be written

$$I(\psi, \eta, d\psi) = \int_{\psi}^{\psi + \psi} \delta(\psi - \phi(x)) d\psi', \quad (A3)$$

from the above three equations we obtain

$$G(\eta, \psi, d\psi) = \int_{\psi}^{\psi + \psi} \int_{\Omega} f(\psi', \eta, \gamma(x)) d\gamma(x) d\psi'$$

$$= d\psi \int_{\Omega} f(\psi, \eta, \gamma(x)) d\gamma(x), \quad (A4)$$

(the last step depending on the continuity of $f$).

An independent expression for $G$ is now obtained in terms of surface statistics. We follow the definitions given in Ref. 125.

The general point in $S(\psi)$ is $x(u, v, \psi)$, where $u$ and $v$ are coordinates used to parametrize the surface. The surface density function is defined by

$$F_\psi(\eta, x; \psi) = \left( \int_{\Omega} \delta(\eta - \gamma(x)) \right. \cdot \delta(x - X(u, v, \psi)) A(u, v, \psi) dudv \right), \quad (A5)$$

where the area ratio between $x$ and $(u,v)$ is

$$A(u, v, \psi) = \left| \frac{\partial X(u, v, \psi)}{\partial u} \times \frac{\partial X(u, v, \psi)}{\partial v} \right|, \quad (A6)$$
and $U$ denotes the region of the parameter space $(u,v)$ corresponding to all points in $S(\phi)$.

The significance of $F_\psi$ is that the surface-to-volume ratio of $S(\phi)$ is given by

$$
\Sigma(\mathbf{x}, \psi) = \int_0^\infty F_\psi(\eta, \mathbf{x}; \psi) d\eta,
$$

(A7)

while the surface pdf of $\gamma$ is

$$
f_\gamma(\eta, \mathbf{x}; \psi) = F_\psi(\eta, \mathbf{x}; \psi) / \Sigma(\mathbf{x}, \psi).
$$

(A8)

It is essential to recognize that $f_\gamma(\eta, \mathbf{x}; \psi)$ is an area-weighted pdf, and hence is different from the (volume-weighted) pdf of $\gamma$, conditional on $\phi(\mathbf{x}) = \psi$.

All points at which the indicator function is unity lie between the surfaces $S(\phi)$ and $S(\phi + d\phi)$ as sketched on Fig. 7. Assuming that the point of interest $X(u,v,\psi)$ is remote from any critical points (at which $\gamma = |\nabla \phi|$ is zero), the distance between these surfaces is

$$
dl(u,v,\psi, d\psi) = d\psi / \gamma(X(u,v,\psi)).
$$

(A9)

Since $dl(u,v,\psi, d\psi)$ is an element of volume between $S(\psi)$ and $S(\psi + d\psi)$, Eq. (A1) can be re-expressed as

$$
G(\eta, \psi, d\psi) = \left\langle \int_0^\infty \delta(\eta - \gamma(\mathbf{x})) dl(u,v,\psi, d\psi) \right\rangle
$$

\[= \frac{d\psi}{\eta} \left\langle \int_0^\infty \delta(\eta - \gamma(\mathbf{x})) A(u,v,\psi) duds \right\rangle
$$

= \frac{d\psi}{\eta} \int_0^\infty F_\psi(\eta, \mathbf{x}; \psi) d\Sigma,

(A10)

where $U_\Omega$ denotes the subset of $U$ corresponding to points $X(u,v,\psi)$ in $\Omega$. The final expression derives from the definition of $F_\psi$ (Eq. A5) and the observation:

$$
\int_\Omega \delta(\mathbf{x} - X[u,v,\psi]) d\mathbf{x} = 1,
$$

(A11)

for $(u,v)$ in $U_\Omega$.

By equating the two expressions for $G$ (eqs. A4 and A10) we obtain

$$
\int_\Omega \{F_\psi(\eta, \mathbf{x}; \psi) - \gamma f(\psi, \eta, \mathbf{x})\} d\mathbf{x} = 0.
$$

(A12)

Since this equation is to be satisfied for arbitrary $\Omega$, it follows that the integrand is zero. Hence, from Eqs. (A7) and (A12) the required results are

$$
\Sigma(\mathbf{x}, \psi) = \int_0^\infty \gamma f(\psi, \eta, \mathbf{x}) d\eta = f_\gamma(\psi; \mathbf{x}) / \langle \gamma(\psi) \rangle,
$$

(A13)

and

$$
f_\gamma(\eta, \mathbf{x}; \psi) = f_{\gamma|\phi}(\eta|\psi; \mathbf{x}) \gamma / \langle \gamma(\psi) \rangle,
$$

(A14)

where $\langle \gamma(\psi) \rangle$ is written for the conditional expectation $\langle \gamma(\mathbf{x})|\phi(\mathbf{x}) = \psi \rangle$, and $f_{\gamma|\phi}$ is the pdf of $\gamma(\mathbf{x})$ conditional on $\phi(\mathbf{x}) = \psi$. It may be seen then that the area-weighted ($f_\gamma$) and volume-weighted ($f_{\gamma|\phi}$) pdf's of $\gamma$ differ by the factor $\gamma / \langle \gamma(\psi) \rangle$.

It is readily shown that this last result can be generalized. Let $\phi(\mathbf{x})$ be any set of random fields—for example, velocities, compositions, or their gradients. Then the surface pdf (on $S(\psi)$) of $\gamma$ and $\phi(\mathbf{x})$ is related to the conditional joint pdf of $\gamma$ and $\phi(\mathbf{x})$ by

$$
f_\gamma(\eta, \phi; \mathbf{x}, \psi) = f_{\gamma|\phi}(\eta|\psi; \mathbf{x}) \eta / \langle \gamma(\psi) \rangle.
$$

(A15)