

Accessed Compositions in Turbulent Reactive Flows

Stephen B. Pope

Sibley School of Mechanical and Aerospace Engineering, Cornell University, Ithaca NY 14853, U.S.A. (pope@mae.cornell.edu)

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Abstract. At a given position and time in a turbulent reactive flow involving many chemical species, the thermochemical composition corresponds to a point in the multi-dimensional composition space. The union of all such points, for all positions and times, is defined to be the accessed region of the composition space. The geometry of the accessed region is investigated from several perspectives. Many existing models of turbulent nonpremixed combustion (e.g., equilibrium chemistry, the steady flamelet model, and the conditional moment closure) implicitly assume that the accessed region is a low-dimensional manifold (of dimension one or two). It is shown from the conservation equations that the simultaneous actions of mixing and reaction can lead to an accessed region of significantly higher dimension than occurs when mixing and reaction act separately or sequentially. For a laminar flame, the accessed region is a curved manifold of the same dimensionality as the flow; whereas for a turbulent reactive flow it is a plane manifold, generally of higher dimension. Several processes are identified which can lead to the edge of the manifold being non-convex.

Keywords: Reactive flows

1. Introduction

In a gas phase reactive flow, the thermochemistry can be described by n_ϕ composition fields $\phi(\mathbf{x}, t) = \{\phi_\alpha(\mathbf{x}, t), \alpha = 1, 2, \dots, n_\phi\}$. For low Mach number flows, these compositions can be taken to be the specific moles of the n_s species and the enthalpy, so that their number is $n_\phi = n_s + 1$. We consider the n_ϕ -dimensional composition space \mathcal{C} , with coordinates $\psi = \{\psi_1, \psi_2, \dots, \psi_{n_\phi}\}$, so that the composition at (\mathbf{x}, t) corresponds to the point $\psi = \phi(\mathbf{x}, t)$. The fundamental question addressed in this paper is: in a turbulent reactive flow, what is the geometry of the accessed region of the composition space? The accessed region, \mathcal{A} , is defined as all compositions that occur (i.e., the union of the points $\psi = \phi(\mathbf{x}, t)$ for all \mathbf{x} and t). Different modelling approaches to turbulent reactive flows (implicitly or explicitly) offer different answers to this question. We give two extreme examples for non-premixed turbulent combustion: the assumed PDF method with equilibrium chemistry (e.g., [7]); and the transported composition PDF method with detailed chemistry (e.g., [5]).



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For two-stream problems (e.g., a fuel jet into an oxidant stream), the mixture fraction $\xi(\mathbf{x}, t)$ is sufficient to determine the elemental composition of the mixture and the enthalpy (provided that radiative heat loss and differential diffusion are negligible). This in turn is sufficient to determine the chemical equilibrium composition, which we denote by $\Phi^{\text{eq}}(\hat{\xi})$, where $\hat{\xi}$ ($0 \leq \hat{\xi} \leq 1$) is an independent mixture fraction variable. By assumption, in the equilibrium-chemistry approach the composition is given by

$$\phi(\mathbf{x}, t) = \Phi^{\text{eq}}(\xi[\mathbf{x}, t]). \quad (1)$$

Thus the accessed region \mathcal{A} of the composition space is (by assumption) the curve (or one-dimensional manifold) $\Phi^{\text{eq}}(\hat{\xi})$, regardless of the dimensionality n_ϕ of the composition space \mathcal{C} .

In contrast, in the transported PDF approach (see e.g., [13]), no assumptions are made about the accessed region, \mathcal{A} . It can, in principle, therefore be coincident with the realizable region. This is defined as the $(n_\phi - 1)$ -dimensional region of the composition space corresponding to non-negative mass fractions which sum to unity, and with the enthalpy corresponding to positive absolute temperatures. In practice, boundary conditions and reaction mechanisms can impose further restrictions (discussed below) which reduce \mathcal{A} ; but in principle any realizable composition is a valid initial or boundary condition and is therefore accessible. Thus, in the absence of information on initial and boundary conditions, all that can be said about the accessed region is that it is contained within the realizable region.

In recent years, PDF calculations have been performed of turbulent flames using detailed mechanisms with of order 20 species [19, 15, 10]; whereas previously, simpler (e.g., four-step) mechanisms had been used, which involve fewer species (e.g., [2]). Mechanisms with of order 500 or even thousands of species have also been proposed (e.g., [16]), and these may be used in future turbulent flame calculations. The increasing number of species considered accentuates the question addressed here: is the accessed region low dimensional (e.g., one or two-dimensional as implied by the equilibrium-chemistry, steady-flamelet, and conditional moment closure models)? Or is its dimensionality of order the number of species as allowed in PDF approaches?

This question is also of paramount importance in the Multiple Mapping Conditioning (MMC) approach recently introduced by Klimenko and Pope [9]. In MMC it is assumed that all compositions are confined to an m -dimensional manifold, where the dimensionality m is prescribed.

In the next section we develop the idea that the accessed region \mathcal{A} is an m -dimensional manifold (for positive integer m), and put existing

models in this framework. In Section 3 we examine idealized situations in which the manifold is clearly identifiable. These cases are: mixing alone; reaction alone; sequential mixing and reaction; and then the general case of simultaneous reaction and mixing. In Section 4 we examine the physical and chemical process that can increase the dimensionality of \mathcal{A} . These are connected with curvature of the manifold and mixing fluctuations. Then in Section 5 we examine the shape of the edge of the manifold and the processes that affect it.

2. Manifolds in Composition Space

By definition, an m -dimensional manifold \mathcal{M} (for $1 \leq m < n_\phi$) in the n_ϕ -dimensional space \mathcal{C} is a smooth geometric object, which locally can be mapped one-to-one to m -dimensional Euclidean space (see, e.g., [17]). At least locally (and sometimes globally) the manifold can be parametrized by m parameters, which we denote by $\boldsymbol{\eta} = \{\eta_1, \eta_2, \dots, \eta_m\}$. Then there is a function $\boldsymbol{\Phi}(\boldsymbol{\eta})$ —which is a mapping from the m -dimensional parameter space to the n_ϕ -dimensional composition space—which describes the compositions on the manifold.

We have already seen that the equilibrium-chemistry assumption corresponds to a one-dimensional manifold \mathcal{M}_{eq} ($m = 1$) parametrized by mixture fraction ($\eta_1 = \hat{\xi}$), i.e., $\boldsymbol{\Phi}^{\text{eq}}(\hat{\xi})$. Similarly, the steady flamelet model [12] (SFM) corresponds to a two-dimensional manifold. According to this model, the composition is uniquely determined by the mixture fraction $\hat{\xi}$ and the scalar dissipation, denoted by $\hat{\chi}$. The composition on the SFM manifold \mathcal{M}_{SFM} is given by

$$\boldsymbol{\Phi}^{\text{SFM}}(\hat{\xi}, \hat{\chi}),$$

and is defined as the composition observed (or calculated) in a specified one-dimensional laminar flame at the given value of mixture fraction, $\hat{\xi}$, and with the value $\hat{\chi}$ of the scalar dissipation at the stoichiometric location. In this case $m = 2$ and $(\eta_1, \eta_2) = (\hat{\xi}, \hat{\chi})$.

In the simplest application of the conditional moment closure [8] (CMC) to non-premixed turbulent combustion, it is assumed that there are no composition fluctuations about their conditional means (conditional on mixture fraction). Hence, by assumption, at (\mathbf{x}, t) the composition is

$$\boldsymbol{\Phi}^{\text{CMC}}(\hat{\xi}, \mathbf{x}, t) = \langle \boldsymbol{\phi}(\mathbf{x}, t) | \xi(\mathbf{x}, t) = \hat{\xi} \rangle. \quad (2)$$

Thus, at given (\mathbf{x}, t) this CMC implies a one-dimensional manifold $\mathcal{M}_{\text{CMC}}(\mathbf{x}, t)$ which is parametrized by $\hat{\xi}$. Notice that in this case the

manifold is local in (\mathbf{x}, t) space—i.e., it is different at different (\mathbf{x}, t) —whereas \mathcal{M}_{eq} and \mathcal{M}_{SFM} are global, independent of (\mathbf{x}, t) . (This distinction between local and global manifolds should not be confused with local and global parametrizations of a manifold.)

To apply these models to turbulent flows it is necessary to know the probability density function (PDF) of the mixture fraction or the joint PDF of mixture fraction and scalar dissipation. More generally, as in MMC, we can consider fields of m parameters, denoted by

$$\boldsymbol{\theta}(\mathbf{x}, t) = \{\theta_1(\mathbf{x}, t), \theta_2(\mathbf{x}, t), \dots, \theta_m(\mathbf{x}, t)\}, \quad (3)$$

and their one-point joint PDF $P(\boldsymbol{\eta}; \mathbf{x}, t)$. Then, if the compositions are confined to the local manifold $\mathcal{M}(\mathbf{x}, t)$ with parametrization $\boldsymbol{\Phi}(\boldsymbol{\eta}, \mathbf{x}, t)$, the joint PDF of $\boldsymbol{\phi}(\mathbf{x}, t)$, $f(\boldsymbol{\psi}; \mathbf{x}, t)$, is given by

$$f(\boldsymbol{\psi}; \mathbf{x}, t) = \int \delta(\boldsymbol{\Phi}[\boldsymbol{\eta}, \mathbf{x}, t] - \boldsymbol{\psi}) P(\boldsymbol{\eta}; \mathbf{x}, t) d\boldsymbol{\eta}, \quad (4)$$

where $\delta(\quad)$ is the n_ϕ -dimensional Dirac delta function and integration is over the whole of the parameter space. This is a fundamental equation in the MMC approach [9]: it shows how the manifold $\boldsymbol{\Phi}(\boldsymbol{\eta}, \mathbf{x}, t)$ maps the distribution in parameter space $\boldsymbol{\eta}$ to the distribution in composition space $\boldsymbol{\psi}$.

3. Implications of Conservation Equations

The statements made above that compositions are confined to low-dimensional manifolds are simply assumptions or assertions in different models. In this section we examine the (simplified) conservation equations to deduce an upper-bound on the geometry of the accessed region \mathcal{A} in idealized circumstances, and then in general.

3.1. INERT MIXING

We consider first the case of inert mixing involving a large number of chemical species. For the general composition variable $\phi_\alpha(\mathbf{x}, t)$ (species specific moles or enthalpy) we consider the conservation equation

$$\frac{D\phi_\alpha}{Dt} \equiv \left(\frac{\partial}{\partial t} + \mathbf{U} \cdot \nabla \right) \phi_\alpha = \Gamma \nabla^2 \phi_\alpha, \quad (5)$$

where $\mathbf{U}(\mathbf{x}, t)$ is the turbulent velocity field. For simplicity we take the density to be constant and uniform: the results obtained below could most likely be generalized to the variable-density case without much

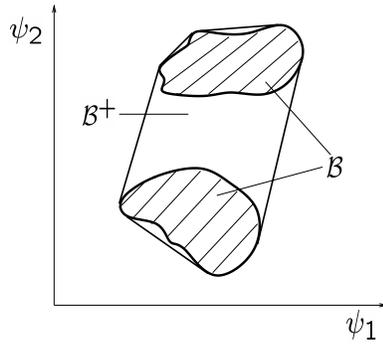


Figure 1. The composition space \mathcal{C} showing the region \mathcal{B} corresponding to initial and boundary conditions and the bounding convex region $\mathcal{B}^+ \equiv \text{hull}(\mathcal{B})$.

difficulty. Much more serious is the assumption embodied in Eq.(5) that the diffusion coefficient Γ is constant, uniform, and the same for each species and enthalpy. Again, the “constant and uniform” assumption could most likely be removed, but the results obtained below depend crucially on the diffusion coefficients being equal. In this regard we make the following observations:

- 1/ As is well known, the effects of differential diffusion and non-unity Lewis number can be substantial in laminar flames (see, e.g., [18]).
- 2/ There is some evidence that these effects are substantially weaker in turbulent non-premixed combustion (e.g., [3]).
- 3/ It is valuable to establish results for the “equal diffusivity” case as a reference against which results with differential diffusion can be compared.

For completeness, we state the known properties of the region of \mathcal{A} of composition space accessed by compositions evolving according to Eq.(5). The region \mathcal{A} is determined by the initial and boundary conditions. Let \mathcal{B} denote the region in composition space corresponding to all initial and boundary conditions. That is, \mathcal{B} is the union of all compositions that occur initially (at $t = 0$) and on the boundary of the domain considered. Then the accessed region \mathcal{A} (which is connected) is bounded by the smallest convex region in \mathcal{C} that contains \mathcal{B} : this region, which we denote by \mathcal{B}^+ , is the *convex hull* of \mathcal{B} , which is also denoted by $\text{hull}(\mathcal{B})$. This is illustrated in Fig. 3.1. (The sketches shown in the figures are, of necessity, in 2D or 3D, but it should be appreciated that they are intended to depict objects in the high-dimensional composition space.)

This result follows simply from three observations. First, if the initial field $\phi(\mathbf{x}, 0)$ contain two adjacent uniform blobs of fluid of composition

ϕ^a and ϕ^b , then, after an infinitesimal time, diffusion between the blobs leads to all compositions along the line segment in \mathcal{C} joining ϕ^a and ϕ^b . Thus, given \mathcal{B} , initial conditions can be found for which the whole of \mathcal{B}^+ is accessed.

Second, it is well known that all global extrema of fields evolving by the convection-diffusion equation Eq.(5) occur on the boundary or in the initial condition (see, e.g., [14]). That is, the actions of convection and diffusion cannot lead to compositions outside \mathcal{B}^+ .

Third, we assume that the flow domain is connected in physical space. That is, given any two points \mathbf{x}^A and \mathbf{x}^B in the flow domain, there is a path connecting them that is everywhere within the fluid. For $t > 0$, the composition fields are continuous, and hence in composition space there is a path connecting $\phi(\mathbf{x}^A)$ to $\phi(\mathbf{x}^B)$. It follows, therefore, that \mathcal{A} is a connected region.

For this case then, the accessed region \mathcal{A} is bounded by \mathcal{B}^+ which is determined by \mathcal{B} . We consider now the accessed regions \mathcal{A} corresponding to different initial and boundary conditions \mathcal{B} .

In general \mathcal{B} is contained in an a -dimensional affine space in \mathcal{C} (with $a < n_\phi$), which we denote as \mathcal{B}^* or $\text{aff}(\mathcal{B})$. An affine space is a subspace which is shifted from the origin by a vector (which is not in the subspace). For example, a 2-dimensional affine space corresponds to a plane that does not intersect the origin. We may also regard \mathcal{B}^* as an a -dimensional plane manifold. It follows that the convex hull \mathcal{B}^+ is also contained in \mathcal{B}^* (i.e., $\text{aff}(\text{hull}(\mathcal{B})) = \text{aff}(\mathcal{B})$), and so the accessed region \mathcal{A} is an a -dimensional plane manifold. Suppose now that \mathcal{B} is contained in an m -dimensional curved manifold in the a -dimensional affine space (for $m < a$). For example, as sketched in Fig. 3.1, \mathcal{B} could be contained in a curve ($m = 1$) in a plane ($a = 2$). It should be appreciated that for this case \mathcal{B}^+ lies in the a -dimensional affine space, but it is not an m -dimensional manifold.

3.2. INERT MIXING OF HOMOGENEOUS STREAMS

In many applications, mixing occurs between a number of inflowing streams, each of which has a fixed uniform composition. Or, we can consider the initial-value problem of the mixing between blobs of fluid of initially uniform composition [4, 6]. In both of these cases, there is a finite number n_b of distinct initial and boundary conditions, and we denote the i -th of these by $\phi^{b,i}$. As illustrated in Fig. 3.2, in composition space \mathcal{C} , the region of initial and boundary conditions \mathcal{B} is just the set of n_b points $\{\psi = \phi^{b,i}, i = 1, 2, \dots, n_b\}$.

In composition space, let m denote the dimensionality of the affine space containing the n_b boundary and initial compositions, i.e., $m \equiv$

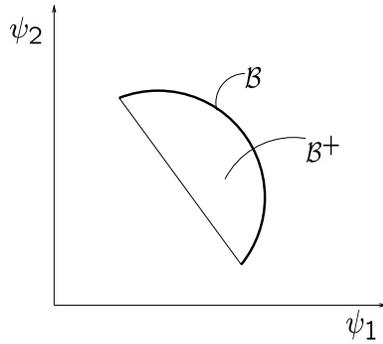


Figure 2. The composition space \mathcal{C} showing the one-dimensional manifold of initial and boundary conditions \mathcal{B} , and the two-dimensional bounding convex region $\mathcal{B}^+ \equiv \text{hull}(\mathcal{B})$.

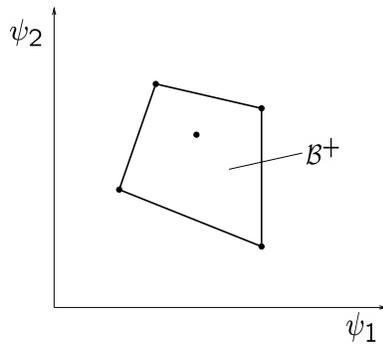


Figure 3. The composition space \mathcal{C} showing initial and boundary conditions (points) corresponding to $n_b = 5$ distinct compositions, $\mathcal{B} = \{\phi^{b,i}, i = 1, 2, \dots, n_b\}$, and the bounding convex region $\mathcal{B}^+ \equiv \text{hull}(\mathcal{B})$.

$\dim(\text{aff}(\mathcal{B}))$. In view of the fact that the species mass fraction sum to unity, we have

$$m \leq \min(n_b, n_\phi) - 1. \quad (6)$$

Without loss of generality, we order the boundary states so that the first $m + 1$ compositions are linearly independent. Evidently, the initial and boundary conditions are contained in the m -dimensional affine space $\mathcal{B}^* = \text{aff}(\mathcal{B})$ which contains $\{\phi^{b,i}, i = 1, 2, \dots, m + 1\}$; and the convex hull $\mathcal{B}^+ \equiv \text{hull}(\mathcal{B})$ is the convex polytope in this m -dimensional affine space whose vertices are a subset of $\{\phi^{b,i}, i = 1, 2, \dots, n_b\}$.

To summarize: for inert mixing between streams or blobs of uniform composition, the accessed region \mathcal{A} is a convex polytope \mathcal{B}^+ in an m -dimensional affine space (or plane manifold). The dimensionality m is one less than the number of linearly independent initial and boundary compositions.

A plane m -dimensional manifold (or affine space) is simply parametrized (globally), and it is constructive to do so in terms of m generalized mixture fractions, denoted by $\theta_p(\mathbf{x}, t)$. In fact, it is convenient to consider $m + 1$ of these mixture fractions (i.e., $p = 1, 2, \dots, m + 1$), but since they sum to unity, only the first m are independent. In the i -th of the $m + 1$ independent streams/blobs, the boundary/initial condition for θ_p is specified as

$$\theta_p^{b,i} = \delta_{pi}, \text{ for } i \leq m + 1. \quad (7)$$

Thus we have, trivially (for $i \leq m + 1$)

$$\phi_\alpha^{b,i} = \sum_{p=1}^{m+1} \phi_\alpha^{b,p} \theta_p^{b,i}. \quad (8)$$

For any linearly dependent streams ($i > m + 1$), by virtue of their linear dependence, there are unique values of $\theta_p^{b,i}$ for which Eq.(8) holds. In other words, Eq.(8) applies to all streams ($i = 1, 2, \dots, n_b$); and it uniquely determines the appropriate boundary conditions $\theta_p^{b,i}$ for $i > m + 1$.

We now specify that $\theta_p(\mathbf{x}, t)$ evolves by Eq.(5), i.e.,

$$\frac{D\theta_p}{Dt} = \Gamma \nabla^2 \theta_p, \quad (9)$$

from the initial and boundary conditions given by Eq.(8). If we define the fields $\hat{\phi}_\alpha(\mathbf{x}, t)$, $\alpha = 1, 2, \dots, n_\phi$, by

$$\hat{\phi}_\alpha(\mathbf{x}, t) \equiv \sum_{p=1}^{m+1} \phi_\alpha^{b,p} \theta_p(\mathbf{x}, t), \quad (10)$$

then it is readily observed that $\hat{\phi}(\mathbf{x}, t)$ satisfies exactly the same initial and boundary conditions and evolution equation as $\phi(\mathbf{x}, t)$, and hence the fields are identical. We also observe that the $m + 1$ mixture fractions sum to unity. Thus, Eq.(10) can be rewritten for $\phi(\mathbf{x}, t)$ as

$$\phi(\mathbf{x}, t) = \phi^{b,m+1} + \sum_{p=1}^m (\phi^{b,p} - \phi^{b,m+1}) \theta_p(\mathbf{x}, t). \quad (11)$$

In summary: for the case of the inert mixing of n_b homogeneous streams or blobs involving n_ϕ compositions, the accessed region \mathcal{A} is a convex polytope \mathcal{B}^+ lying in an m -dimensional plane manifold, where m is one less than the number of linearly independent streams or blobs. This manifold can be parametrized by m independent mixture fractions: the mapping $\Phi^{\text{MIX}}(\boldsymbol{\eta})$ between the m -dimensional parameter space and the n_ϕ -dimensional compositions is linear, i.e.,

$$\Phi^{\text{MIX}}(\boldsymbol{\eta}) = \boldsymbol{\phi}^{b,m+1} + \mathbf{H}\boldsymbol{\eta}, \quad (12)$$

where the $n_\phi \times m$ matrix \mathbf{H} is given by

$$H_{\alpha p} = \phi_\alpha^{b,p} - \phi_\alpha^{b,m+1}, \quad (13)$$

cf. Eq.(11). Thus, the n_ϕ composition fields $\boldsymbol{\phi}(\mathbf{x}, t)$ can be determined from the m mixture fraction fields $\boldsymbol{\theta}(\mathbf{x}, t)$ by

$$\boldsymbol{\phi}(\mathbf{x}, t) = \Phi^{\text{MIX}}(\boldsymbol{\theta}[\mathbf{x}, t]) = \boldsymbol{\phi}^{b,m+1} + \mathbf{H}\boldsymbol{\theta}(\mathbf{x}, t). \quad (14)$$

For the simplest case of the inert mixing between a fuel stream (of composition $\boldsymbol{\phi}^{fu}$) and an oxidant stream (of composition $\boldsymbol{\phi}^{ox}$), we have $n_b = 2$, $m = 1$, and Eq. (14) becomes

$$\boldsymbol{\phi}(\mathbf{x}, t) = \Phi^{\text{MIX}}(\xi[\mathbf{x}, t]) = \boldsymbol{\phi}^{ox} + (\boldsymbol{\phi}^{fu} - \boldsymbol{\phi}^{ox})\xi(\mathbf{x}, t), \quad (15)$$

where $\xi(\mathbf{x}, t) \equiv \theta_1(\mathbf{x}, t)$ is the usual mixture fraction, which is unity in the fuel stream and zero in the oxidant stream.

3.3. HOMOGENEOUS REACTION

Next we consider the case of homogeneous, adiabatic, isobaric reaction from a given initial condition. For this case, the composition $\boldsymbol{\phi}(t)$ depends only on time, and it evolves by the ordinary differential equation

$$\frac{d\boldsymbol{\phi}_\alpha}{dt} = \mathbf{S}_\alpha(\boldsymbol{\phi}[t]), \quad (16)$$

where \mathbf{S} denotes the rate of change due to chemical reaction, which is a known function of the composition.

The composition space \mathcal{C} can be decomposed into two sub-spaces: the conserved subspace \mathcal{C}_C and the reactive subspace \mathcal{C}_R . During chemical reactions both enthalpy and elements are conserved. Thus, the conserved subspace is (at least) $(n_e + 1)$ -dimensional, where n_e is the number of elements. The species are represented as specific moles (mass fraction divided by molecular weight) so that the two subspaces are orthogonal. We denote by n_C and n_R their dimensionality, obviously with $n_C + n_R = n_\phi$. Every vector in composition space can be decomposed into a component in the conserved subspace and a component in the reactive subspace [11], e.g.,

$$\boldsymbol{\phi} = \boldsymbol{\phi}^C + \boldsymbol{\phi}^R, \quad (17)$$

and

$$\mathbf{S} = \mathbf{S}^C + \mathbf{S}^R, \quad (18)$$

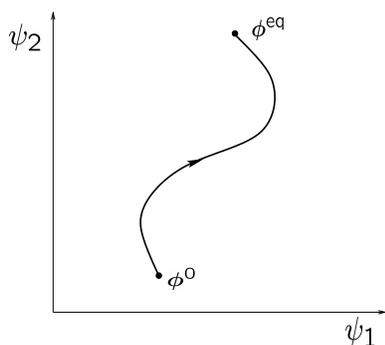


Figure 4. Trajectory in composition space corresponding to homogeneous reaction: ϕ^0 and ϕ^{eq} denote the initial condition and the corresponding equilibrium composition.

where (by definition of \mathcal{C}_R) \mathbf{S}^C is zero. Thus Eq.(16) can be decomposed as

$$\begin{aligned} \frac{d\phi^C}{dt} &= 0, \\ \frac{d\phi^R}{dt} &= \mathbf{S}(\phi). \end{aligned} \quad (19)$$

From a given initial condition, $\phi(0) = \phi^0$, the solution to Eq.(16) (or, equivalently, Eq.(19)) is a trajectory in composition space, from the initial point $\psi = \phi^0$ to the point corresponding to chemical equilibrium $\psi = \phi^{\text{eq}}$, see Fig. 3.3. The conserved component does not change, i.e., $\phi^C(t) = \phi^{0C} \equiv \phi^C(0)$, and consequently composition differences $\phi(t_2) - \phi(t_1)$ are vectors in the reactive subspace. The equilibrium composition ϕ^{eq} is uniquely determined by ϕ^{0C} .

We define the *reaction mapping* $\mathbf{R}(\phi^0, t)$ to be the solution after time t of Eq.(16) from the initial condition $\phi(0) = \phi^0$. Thus the reaction trajectory is $\mathbf{R}(\phi^0, t)$ for fixed ϕ^0 and all $t \geq 0$; and the equilibrium composition corresponding to ϕ^0 is $\phi^{\text{eq}} = \mathbf{R}(\phi^0, \infty)$.

The reaction trajectory is a curve (i.e., a one-dimensional manifold) that can be parametrized by time, by arclength, by entropy, or by any other quantity which varies monotonically along it. Thus, for this problem, the accessed region \mathcal{A} is a one-dimensional manifold, regardless of the number of species.

An important issue is the dimensionality (denoted by n'_R) of the affine space containing the reaction trajectory. If the trajectory is a line segment (and hence has no curvature) then $n'_R = 1$. In general we have $1 \leq n'_R \leq n_R$.

3.4. SEQUENTIAL MIXING AND REACTION

We now consider the hypothetical case in which mixing alone occurs (via Eq.(5)) for some time, and then reaction alone occurs (via Eq.(16)) for some time.

As discussed in Section 3.1, if the boundary and initial conditions are contained in the region \mathcal{B} of composition space, then the accessed region after mixing, \mathcal{A}_m , is the convex hull of \mathcal{B} , which is denoted by $\mathcal{B}^+ \equiv \text{hull}(\mathcal{B})$. Let $n_{\mathcal{B}}$ denote the dimensionality of the affine space $\mathcal{B}^* \equiv \text{aff}(\mathcal{B})$ containing \mathcal{B} (and hence also \mathcal{B}^+). Let $\phi^{\text{mix}}(\mathbf{x})$ denote the composition field after mixing has occurred. Then, for all \mathbf{x} , in composition space $\phi^{\text{mix}}(\mathbf{x})$ is in the accessed region \mathcal{A}_m which lies in the $n_{\mathcal{B}}$ -dimensional affine space \mathcal{B}^* .

Starting from the composition field $\phi^{\text{mix}}(\mathbf{x})$, and with time reset to $t = 0$, now consider reaction occurring (without diffusion). The result is the same whether we consider the fluid to be at rest and reacting by

$$\frac{d\phi}{dt} = \mathbf{S}(\phi), \quad (20)$$

or whether we consider it be convected and reacting by

$$\frac{D\phi}{Dt} = \mathbf{S}(\phi). \quad (21)$$

For definiteness and simplicity we consider the former. Thus, for each \mathbf{x} in the flow domain, the composition evolves by Eq.(20) from the initial condition $\phi^{\text{mix}}(\mathbf{x})$.

The composition at time t is given by the reaction mapping as

$$\phi(\mathbf{x}, t) = \mathbf{R}(\phi^{\text{mix}}(\mathbf{x}), t). \quad (22)$$

Our focus here is on the region \mathcal{A}_{mr} accessed by compositions $\phi(\mathbf{x}, t)$ for all \mathbf{x} in the domain and all $t \geq 0$. This is just the *reaction-mapped region* generated by $\mathcal{A}_m = \mathcal{B}^+$ which we denote by $(\mathcal{B}^+)_{\mathcal{R}}$ or $\mathcal{R}(\mathcal{B}^+)$, and define by

$$\mathcal{R}(\mathcal{B}^+) \equiv \{\mathbf{R}(\psi, t) : \psi \in \mathcal{B}^+, t \geq 0\}. \quad (23)$$

Figure 3.4 shows a sketch of $\mathcal{A}_{mr} = \mathcal{R}(\mathcal{B}^+)$ for a particular case. (As discussed below, several qualitatively different behaviors are possible.) The sketch shows reaction trajectories emanating from \mathcal{B}^+ and terminating at the *equilibrium region*, denoted by $\mathcal{B}_{\text{eq}}^+$. As may be observed, the accessed region is bounded by (a) part of the boundary of \mathcal{B}^+ (b) reaction trajectories from the boundary of \mathcal{B}^+ , and (c) the equilibrium region $\mathcal{B}_{\text{eq}}^+$. Whereas \mathcal{B}^+ is convex, it may be observed that $(\mathcal{B}^+)_{\mathcal{R}}$ may

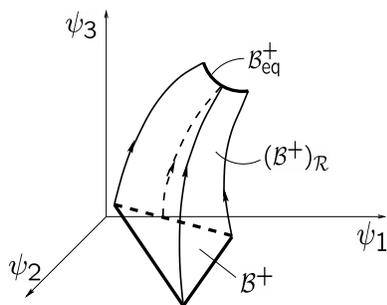


Figure 5. Sketch of the reaction-mapped region $(\mathcal{B}^+)_{\mathcal{R}} = \mathcal{R}(\mathcal{B}^+)$ generated by \mathcal{B}^+ showing the equilibrium region \mathcal{B}_{eq}^+ . (For this case $\dim(\mathcal{B}_{eq}^+) = n_C = 1$; $n_R = 2$ and $n_B = 2$.)

be non-convex due either to the reaction trajectories being curved or non-parallel, or to the equilibrium region being non-convex.

The geometry of $\mathcal{A}_{mr} = (\mathcal{B}^+)_{\mathcal{R}}$ depends on the relationship between two subspaces, now defined: the *initial tangent space* \mathcal{B}^0 ; and the *accessed reactive subspace* \mathcal{C}'_R .

The initial tangent space, which is determined by the initial and boundary conditions, is the space spanned by $\phi^{\text{mix}}(\mathbf{x}) - \phi^{\text{mix}}(0)$: it is simply the affine space \mathcal{B}^* containing \mathcal{B} and \mathcal{B}^+ translated to the origin, and hence is n_B -dimensional. All composition differences $\phi^{\text{mix}}(\mathbf{x}^A) - \phi^{\text{mix}}(\mathbf{x}^B)$ are in \mathcal{B}^0 .

The accessed reactive subspace \mathcal{C}'_R is defined to be the subspace spanned by the reaction vectors $\mathbf{S}(\phi(\mathbf{x}, t))$ for all \mathbf{x}, t . Clearly this is a subspace of the reactive subspace \mathcal{C}_R , and hence its dimensionality, n'_R , is less than or equal to n_R . Other significances of \mathcal{C}'_R are that it is the tangent bundle of the trajectories $\mathbf{R}(\phi^{\text{mix}}(\mathbf{x}), t)$, and that the composition increments

$$\phi(\mathbf{x}, t) - \phi(\mathbf{x}, 0) = \mathcal{R}(\phi^{\text{mix}}(\mathbf{x}), t) - \phi^{\text{mix}}(\mathbf{x}) \quad (24)$$

are elements of \mathcal{C}'_R .

The initial compositions $\phi(\mathbf{x}, 0) = \phi^{\text{mix}}(\mathbf{x})$ are in the affine space \mathcal{B}^* ; and the composition increments $\phi(\mathbf{x}, t) - \phi(\mathbf{x}, 0)$ are in the accessed reactive subspace \mathcal{C}'_R . Thus for the affine space $\mathcal{A}^*_{mr} \equiv \text{aff}(\mathcal{A}_{mr})$ containing the compositions $\phi(\mathbf{x}, t)$ we have

$$\dim(\mathcal{A}^*_{mr}) = \dim(\mathcal{B}^0 \cup \mathcal{C}'_R), \quad (25)$$

and hence

$$\max(n_B, n'_R) \leq \dim(\mathcal{A}^*_{mr}) \leq n_B + n'_R. \quad (26)$$

Two extreme cases can be considered. First, it could be that all reaction vectors $\mathbf{S}(\phi(\mathbf{x}, t))$ are in the tangent space \mathcal{B}^0 . In this case

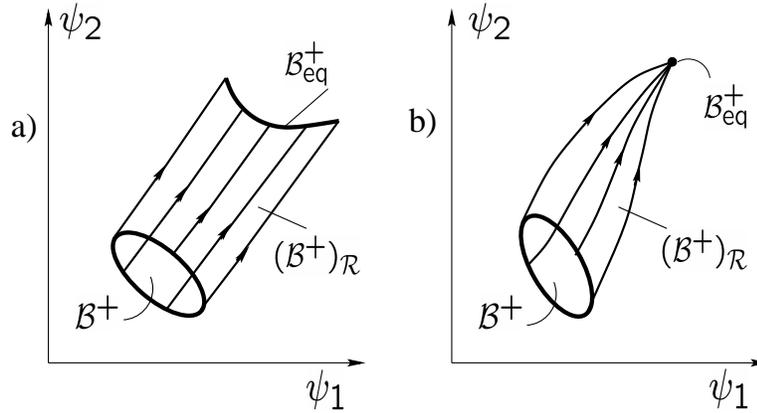


Figure 6. Sketches of $\mathcal{A}_{mr} = (\mathcal{B}^+)_{\mathcal{R}}$ for cases in which the accessed reactive space is a subspace of the tangent space: (a) $n'_R = 1$ in which case trajectories are parallel line segments, and (b) $n'_R = 2$.

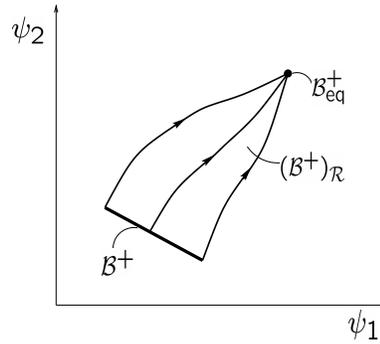


Figure 7. Sketch of the accessed region $\mathcal{A}^{mr} = (\mathcal{B}^+)_{\mathcal{R}}$ for a case in which \mathcal{C}'_R and \mathcal{B}_0 are disjoint.

reaction does not increase the dimensionality of the accessed region. Instead we have

$$\mathcal{A}_{mr}^* = \mathcal{A}_m^* = \mathcal{B}^*. \quad (27)$$

This case is illustrated in Fig. 3.4, in which both \mathcal{B}^+ and $(\mathcal{B}^+)_{\mathcal{R}}$ are two-dimensional. In the second extreme case, \mathcal{B}^0 and \mathcal{C}'_R are disjoint so that no reaction vector \mathbf{S} is in the tangent space \mathcal{B}^0 . In this case, illustrated in Fig. 3.4, compared to \mathcal{A}_m , the dimensionality of \mathcal{A}_{mr} is increased by one; but the dimensionality of the affine space is increased by n'_R .

3.5. SIMULTANEOUS MIXING AND REACTION

The case of most interest is, of course, when mixing and reaction occur simultaneously according to the equation

$$\frac{D\phi}{Dt} = \Gamma \nabla^2 \phi + \mathbf{S}(\phi). \quad (28)$$

We consider in this section the accessed region \mathcal{A} of the composition $\phi(\mathbf{x}, t)$ given by Eq.(28) with initial and boundary conditions in region \mathcal{B} of the composition space \mathcal{C} .

It is clear from the discussion in the preceding subsections that an upper bound on \mathcal{A} is as follows [13]:

The accessed region \mathcal{A} is (or is contained within) the smallest convex region in \mathcal{C} which contains \mathcal{B} , and on the boundary of which the reaction vector \mathbf{S} are inward pointing (or tangent to the boundary).

As we have seen, mixing can “fill in” a non-convex region, but it cannot extend a convex region. Reaction trajectories pass from inside a convex region to its exterior if, and only if, the reaction vector \mathbf{S} is outward pointing on the boundary. (Note that \mathcal{B} is contained in the realizable region, on the boundary of which reaction vectors are inward-pointing or tangent to the boundary. Hence, \mathcal{A} is contained in the realizable region.)

The accessed region \mathcal{A} identified above is convex, so that $\text{hull}(\mathcal{A}) = \mathcal{A}$, and it is a reaction-mapped region so that it contains no outward pointing vectors \mathbf{S} and $\mathcal{R}(\mathcal{A}) = \mathcal{A}$. It then follows that \mathcal{A} contains \mathcal{B} and satisfies the relation

$$\text{hull}(\mathcal{R}(\mathcal{A})) = \mathcal{R}(\text{hull}(\mathcal{A})), \quad (29)$$

and indeed \mathcal{A} can be defined as the smallest region that has these properties. Note that Eq.(29) does not hold for a general region. In particular, the accessed region \mathcal{A}_{mr} for sequential mixing then reaction

$$\mathcal{A}_{mr} = \mathcal{R}(\text{hull}(\mathcal{B})) = (\mathcal{B}^+)_{\mathcal{R}}, \quad (30)$$

may not be convex; and the accessed region \mathcal{A}_{rm} for sequential reaction then mixing

$$\mathcal{A}_{rm} = \text{hull}(\mathcal{R}(\mathcal{B})) = (\mathcal{B}_{\mathcal{R}})^+, \quad (31)$$

may have outward pointing vectors \mathbf{S} . The accessed region \mathcal{A} satisfying Eq.(29) can be obtained by iterating $\text{hull}(\mathcal{R}(\cdot))$ on \mathcal{B} .

4. Composition Evolution on Manifolds

As in the preceding subsection, we consider the accessed region \mathcal{A} of the composition $\phi(\mathbf{x}, t)$ evolving by the reaction-convection-diffusion equation Eq.(28) with initial and boundary conditions in region \mathcal{B} of the composition space.

It is important to appreciate that the result for \mathcal{A} obtained in Section 3.5 is an upper bound. Consider for example a steady, two-dimensional laminar flame involving 100 species, and with arbitrarily complicated boundary conditions. The bound on \mathcal{A} given in Section 3.5 is an affine space of dimension most likely more than 90. But in fact, \mathcal{A} is a two-dimensional manifold: for the compositions that occur can be parametrized by the two spatial coordinates, i.e., $\phi(x_1, x_2)$.

A limitation of the analysis in Section 3.5 is that it does not allow for the possibility of the combined effects of diffusion and reaction to restrict compositions to a non-convex region.

4.1. TANGENT AND NORMAL SPACE DECOMPOSITION

To explore these effects, we perform here a different kind of analysis. We suppose that at time t_0 the compositions are confined to an m -dimensional global manifold \mathcal{M} . The compositions on \mathcal{M} are given by $\Phi(\boldsymbol{\eta})$ which is a mapping from the m -dimensional parameter space to the n_ϕ -dimensional composition space. There are parameter fields $\boldsymbol{\theta}(\mathbf{x}, t) = \{\theta_1(\mathbf{x}, t), \theta_2(\mathbf{x}, t), \dots, \theta_m(\mathbf{x}, t)\}$ such that the composition at time t_0 is

$$\phi(\mathbf{x}, t_0) = \Phi(\boldsymbol{\theta}(\mathbf{x}, t_0)). \quad (32)$$

We then use the composition evolution equation, Eq.(28), to determine if $\phi(\mathbf{x}, t)$ remains on the manifold, or to identify the processes that cause it to leave the manifold.

Within the framework of this analysis many different questions can be addressed, because neither the manifold \mathcal{M} nor its parametrization $\Phi(\boldsymbol{\eta})$ have been specified.

We consider an arbitrary fixed location \mathbf{x}_0 at time t_0 , and define

$$\boldsymbol{\theta}_0 \equiv \boldsymbol{\theta}(\mathbf{x}_0, t_0). \quad (33)$$

The compositions in an infinitesimal neighborhood of \mathbf{x}_0 are given by $\Phi(\boldsymbol{\eta})$ in an infinitesimal neighborhood of $\boldsymbol{\eta} = \boldsymbol{\theta}_0$.

The set of m tangent vectors

$$\mathbf{T}_p \equiv \left(\frac{\partial \Phi}{\partial \eta_p} \right)_{\boldsymbol{\eta}=\boldsymbol{\theta}_0}, \quad (34)$$

span the tangent space at $\boldsymbol{\theta}_0$, which is denoted by \mathcal{T} ; and the normal space \mathcal{N} is the orthogonal complement of \mathcal{T} . Every vector \mathbf{V} in composition space can be decomposed as

$$\mathbf{V} = \mathbf{V}^{\parallel} + \mathbf{V}^{\perp}, \quad (35)$$

where \mathbf{V}^{\parallel} is in \mathcal{T} , and \mathbf{V}^{\perp} is in \mathcal{N} . We are particularly interested in the rate of change of composition:

$$\begin{aligned} \left(\frac{\partial\phi}{\partial t}\right)_{\mathbf{x}_0,t_0} &= \left(\frac{\partial\phi}{\partial t}\right)_{\mathbf{x}_0,t_0}^{\parallel} + \left(\frac{\partial\phi}{\partial t}\right)_{\mathbf{x}_0,t_0}^{\perp} \\ &= \dot{\phi}^{\parallel} + \dot{\phi}^{\perp}, \end{aligned} \quad (36)$$

where the second line introduces an abbreviated notation. In composition space, $\dot{\phi}^{\parallel}$ represents motion along the manifold, whereas $\dot{\phi}^{\perp}$ represents motion perpendicular to the manifold (in a normal direction). Hence, if $\dot{\phi}^{\perp}$ is zero (for all \mathbf{x}_0 and t_0) the composition remains on the manifold \mathcal{M} , which is therefore identified as being (or containing) the accessed region \mathcal{A} .

4.2. MOTION IN THE TANGENT AND NORMAL DIRECTIONS

Expressions for $\dot{\phi}^{\parallel}$ and $\dot{\phi}^{\perp}$ are obtained from Eq.(28), which is rewritten as

$$\frac{\partial\phi}{\partial t} = -U_i \frac{\partial\phi}{\partial x_i} + \Gamma \nabla^2 \phi + \mathbf{S}. \quad (37)$$

For the composition gradient (at \mathbf{x}_0, t_0), the chain rule yields

$$\begin{aligned} \frac{\partial\phi}{\partial x_i} &= \frac{\partial}{\partial x_i} \Phi(\boldsymbol{\theta}[\mathbf{x}, t]) \\ &= \frac{\partial\Phi}{\partial\eta_p} \frac{\partial\theta_p}{\partial x_i} = \mathbf{T}_p \frac{\partial\theta_p}{\partial x_i}, \end{aligned} \quad (38)$$

where summation over repeated indexes is implied; and, here and below, it is understood that all quantities are evaluated at $(\mathbf{x}, t, \boldsymbol{\eta}) = (\mathbf{x}_0, t_0, \boldsymbol{\theta}_0)$. The final expression in Eq.(38) is clearly a vector in the tangent space \mathcal{T} , so that we have

$$\left(\frac{\partial\phi}{\partial x_i}\right)^{\parallel} = \mathbf{T}_p \frac{\partial\theta_p}{\partial x_i}, \quad (39)$$

$$\left(\frac{\partial\phi}{\partial x_i}\right)^{\perp} = 0. \quad (40)$$

Thus, as is well known, convection does not cause the composition to leave the manifold, however \mathcal{M} is defined. (This result is obvious from the Lagrangian perspective.)

For the Laplacian we obtain (from Eq.(38))

$$\nabla^2 \phi = \frac{\partial}{\partial x_i} \left[\frac{\partial\Phi}{\partial\eta_p} \frac{\partial\theta_p}{\partial x_i} \right]$$

$$= \frac{\partial \Phi}{\partial \eta_p} \nabla^2 \theta_p + \frac{\partial^2 \Phi}{\partial \eta_p \partial \eta_q} \frac{\partial \theta_p}{\partial x_i} \frac{\partial \theta_q}{\partial x_i}. \quad (41)$$

Thus, with the definitions

$$\mathbf{K}_{pq} \equiv \left(\frac{\partial^2 \Phi}{\partial \eta_p \partial \eta_q} \right)_{\boldsymbol{\eta}=\boldsymbol{\theta}_0}, \quad (42)$$

and

$$\chi_{pq} \equiv \Gamma \frac{\partial \theta_p}{\partial x_i} \frac{\partial \theta_q}{\partial x_i}, \quad (43)$$

the diffusion term in Eq.(37) can be written

$$\Gamma \nabla^2 \phi = \mathbf{T}_p \Gamma \nabla^2 \theta_p + \mathbf{K}_{pq} \chi_{pq}. \quad (44)$$

Clearly the first term on the right-hand side of Eq.(44) is a vector in the tangent space; whereas in general $\mathbf{K}_{pq} = \mathbf{K}_{pq}^{\parallel} + \mathbf{K}_{pq}^{\perp}$ has components in both the tangent and normal spaces. If the manifold is curved at ϕ_0 , then \mathbf{K}_{pq}^{\perp} is non-zero for some p and q ; whereas, if the manifold is not curved, then \mathbf{K}_{pq}^{\perp} is zero for all p and q .

The above results, together with the decomposition $\mathbf{S} = \mathbf{S}^{\parallel} + \mathbf{S}^{\perp}$, can be substituted into Eq.(36), to obtain an expression for $(\partial \phi / \partial t)_{\mathbf{x}_0, t_0}$. When decomposed into components in \mathcal{T} and \mathcal{N} , the results are:

$$\dot{\phi}^{\parallel} = \left(\frac{\partial \phi}{\partial t} \right)^{\parallel} = \mathbf{T}_p (-\mathbf{U} \cdot \nabla \theta_p + \Gamma \nabla^2 \theta_p) + \mathbf{K}_{pq}^{\parallel} \chi_{pq} + \mathbf{S}^{\parallel}, \quad (45)$$

and

$$\dot{\phi}^{\perp} = \left(\frac{\partial \phi}{\partial t} \right)^{\perp} = \mathbf{K}_{pq}^{\perp} \chi_{pq} + \mathbf{S}^{\perp}. \quad (46)$$

This last equation is the key result of this development, and its implications are explored in the different circumstances in the following subsections.

(It may be observed that the form of Eq.(46) is quite similar to the fundamental equations in the steady flamelet model, in CMC, and in the quasi-equilibrium distributed reaction (QEDR) model [1].)

4.3. MOTION IN THE NORMAL DIRECTION

We consider here the circumstances in which $\dot{\phi}^{\perp}$ is zero, so that compositions are confined to the manifold \mathcal{M} . The conditions are simply that the right-hand side of Eq.(46) vanishes, i.e.,

$$\dot{\phi}^{\perp} = \mathbf{S}^{\perp} + \mathbf{K}_{pq}^{\perp} \chi_{pq} = 0, \quad (47)$$

or in a fuller notation

$$\left(\frac{\partial\phi}{\partial t}\right)_{\mathbf{x}_0,t_0}^\perp = \mathbf{S}(\Phi(\boldsymbol{\theta}_0))^\perp + \left(\frac{\partial^2\Phi(\boldsymbol{\eta})}{\partial\eta_p\partial\eta_q}\right)_{\boldsymbol{\eta}=\boldsymbol{\theta}_0}^\perp \Gamma\left(\frac{\partial\theta_p}{\partial x_i}\frac{\partial\theta_q}{\partial x_i}\right)_{\mathbf{x}_0,t_0} = 0. \quad (48)$$

If \mathcal{M} is an affine space, then \mathbf{K}_{pq}^\perp is zero. If \mathcal{M} is a reaction-mapped region, then \mathbf{S}^\perp is zero. Thus, consistent with our previous observations, if \mathcal{M} is a convex reaction-mapped region, then $\dot{\phi}^\perp$ is zero, and compositions remain in \mathcal{M} . However, if \mathbf{K}_{pq}^\perp is zero and \mathbf{S}^\perp is non-zero, then Eq.(47) cannot be balanced, and reaction causes compositions to leave the manifold in a normal direction, causing the dimensionality of the accessed region to increase. In the case that \mathbf{S}^\perp is zero but \mathbf{K}_{pq}^\perp is non-zero, the possibility that $\mathbf{K}_{pq}^\perp\chi_{pq}$ is zero cannot immediately be ruled out. But, for reasons deduced below, in a turbulent flow $\mathbf{K}_{pq}^\perp\chi_{pq}$ is non-zero, and so Eq.(47) is not balanced, and mixing causes compositions to leave the manifold.

For any manifold \mathcal{M} , the structure of Eq.(47) and Eq.(48) is that \mathbf{S}^\perp and \mathbf{K}_{pq}^\perp are known functions of the manifold at $\boldsymbol{\theta}_0$ (with no direct dependence on \mathbf{x} and t) whereas χ_{pq} depends on local spatial gradients of the parameters $\boldsymbol{\theta}(\mathbf{x}, t)$. If \mathbf{S}^\perp is non-zero, the only way that the equation can balance, is if χ_{pq} is a unique function of $\boldsymbol{\theta}_0$. Thinking of the case of turbulent flow (in which $\boldsymbol{\theta}(\mathbf{x}, t)$ are random fields), this condition is satisfied only if χ_{pq} has no (conditional) fluctuations about its conditional mean, which must be spatially and temporally uniform, i.e.,

$$\chi_{pq}(\mathbf{x}_0, t) = \langle\chi_{pq}|\boldsymbol{\theta}_0\rangle, \quad (49)$$

with

$$\langle\chi_{pq}|\boldsymbol{\theta}_0\rangle \equiv \langle\chi_{pq}(\mathbf{x}, t)|\boldsymbol{\theta}(\mathbf{x}, t) = \boldsymbol{\theta}_0\rangle, \quad (50)$$

being independent of \mathbf{x} and t . If these conditions are satisfied, then all terms in Eq.(47) depend solely on $\boldsymbol{\theta}_0$. Thus Eq.(49) is a necessary condition for $\dot{\phi}^\perp$ to be zero, when \mathbf{S}^\perp is non-zero.

To illustrate this result, consider first a steady, three-dimensional laminar flame. In this case there is a three-dimensional manifold, which can be parametrized by $\mathbf{x} = \{x_1, x_2, x_3\}$:

$$\boldsymbol{\theta} = \mathbf{x}, \quad \phi(\mathbf{x}) = \Phi(\boldsymbol{\theta}). \quad (51)$$

With $\boldsymbol{\theta} = \mathbf{x}$, from the definition of χ_{pq} (Eq. 43) we obtain simply

$$\chi_{pq} = \Gamma\delta_{pq}, \quad (52)$$

which is a (trivial) function of $\boldsymbol{\theta}$. Thus, Eq.(48) is satisfied, and in fact it reduces to

$$(\mathbf{S} + \Gamma \nabla^2 \phi)^\perp = 0. \quad (53)$$

For the turbulent case, it seems that Eq.(49) cannot be satisfied: for it requires that the parameters θ characterize their own dissipation. To illustrate this point, consider nonpremixed turbulent combustion, and let the single parameter $\eta_1 = \hat{\xi}$ correspond to mixture fraction, the field of which is $\theta_1(\mathbf{x}, t) = \xi(\mathbf{x}, t)$. For this case, Eq.(48) becomes

$$\dot{\phi}^\perp = \mathbf{S}(\Phi(\xi_0))^\perp + \left(\frac{\partial^2 \Phi(\hat{\xi})}{\partial \hat{\xi}^2} \right)_{\hat{\xi}=\xi_0}^\perp \frac{1}{2} \chi(\mathbf{x}_0, t_0), \quad (54)$$

where ξ_0 is defined by $\xi_0 \equiv \xi(\mathbf{x}_0, t_0)$, and χ is the scalar dissipation

$$\chi \equiv 2\Gamma \nabla \xi \cdot \nabla \xi. \quad (55)$$

According to Eq.(54), $\dot{\phi}^\perp$ can be zero only if there are no scalar dissipation fluctuations about the condition mean, which must be uniform, i.e.,

$$\chi(\mathbf{x}_0, t_0) = \langle \chi | \xi_0 \rangle, \quad (56)$$

where

$$\langle \chi | \hat{\xi} \rangle \equiv \langle \chi(\mathbf{x}, t) | \xi(\mathbf{x}, t) = \hat{\xi} \rangle, \quad (57)$$

is independent of \mathbf{x}, t . Needless to say, neither Eq.(56) nor Eq.(57) is satisfied for a turbulent flow. (It may be noted, however, that these equations are satisfied for a 1D steady, laminar flow in which $\xi(x)$ varies monotonically with the spatial coordinate, x .)

It is evident, then, that for turbulent nonpremixed combustion, the accessed region cannot be parametrized by mixture fraction alone, since χ is not determined by ξ . It is natural to consider a two-dimensional manifold parametrized by mixture fraction and scalar dissipation, $(\eta_1, \eta_2) = (\hat{\xi}, \hat{\chi})$, with parameter fields $\xi(\mathbf{x}, t)$ and $\chi(\mathbf{x}, t)$. For this case, Eq.(48) becomes

$$\begin{aligned} \dot{\phi}^\perp &= \mathbf{S}(\Phi(\xi_0, \chi_0))^\perp + \left(\frac{\partial^2 \Phi}{\partial \hat{\xi}^2} \right)^\perp \frac{1}{2} \chi_0 \\ &+ \left(\frac{\partial^2 \Phi}{\partial \hat{\xi} \partial \hat{\chi}} \right)^\perp 2\Gamma \nabla \xi \cdot \nabla \chi + \left(\frac{\partial^2 \Phi}{\partial \hat{\chi}^2} \right)^\perp \Gamma \nabla \chi \cdot \nabla \chi, \end{aligned} \quad (58)$$

where $\chi_0 \equiv \chi(\mathbf{x}_0, t_0)$ and all quantities are evaluated at $(\mathbf{x}, t, \hat{\xi}, \hat{\chi}) = (\mathbf{x}_0, t_0, \xi_0, \chi_0)$. It may be seen that introducing $\hat{\chi}$ as a parameter is successful in making the first mixing term in Eq.(58) depend solely on the parameters ξ_0 and χ_0 . But in so doing, the additional mixing terms involving $\nabla \xi \cdot \nabla \chi$ and $\nabla \chi \cdot \nabla \chi$ are introduced, which (in general) are not known in terms of these parameters.

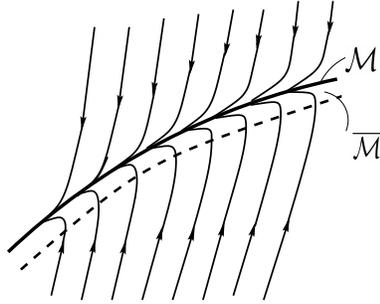


Figure 8. Sketch of a curved intrinsic low-dimensional manifold (ILDm) \mathcal{M} showing reaction trajectories. Compositions are confined to the region $\overline{\mathcal{M}}$ close to \mathcal{M} .

A conclusion from the above considerations is that, for turbulent reactive flows, compositions cannot be confined to manifolds with curvature, because reaction \mathbf{S}^\perp and mixing $\mathbf{K}_{pq}^\perp \chi_{pq}$ cannot exactly balance in the presence of (conditional) fluctuations in χ_{pq} .

This conclusion notwithstanding, it is highly likely that in some circumstances compositions lie very close to strongly attracting intrinsic low-dimensional manifolds (ILDm) [11]. As sketched in Fig. 4.3, in the absence of mixing, reaction rapidly transports compositions to the ILDM, on which \mathbf{S}^\perp is (approximately) zero. Because of the manifold's curvature, mixing tends to draw compositions off the manifold; but (for a strongly attracting manifold) \mathbf{S}^\perp increases rapidly as compositions depart from the manifold and hence a balance between reaction and mixing can be established in a narrow region around \mathcal{M} . This region is denoted by $\overline{\mathcal{M}}$ in Fig. 4.3. If all of the principal curvatures of the manifold are of the same sign, then $\overline{\mathcal{M}}$ is on one side of \mathcal{M} , as depicted in Fig. 4.3. Otherwise $\overline{\mathcal{M}}$ is on both sides of \mathcal{M} . (This behavior is an example of “strong inward reaction” which is discussed in the next section.)

5. Motion in the Edge Direction

The m -dimensional manifold \mathcal{M} that we are considering is, more precisely, a “manifold with edge” [17]. That is, as sketched in Fig. 5, the manifold \mathcal{M} has a boundary or edge, which we denote by $\partial\mathcal{M}$.

In the simplest case (sketched in Fig. 5), $\partial\mathcal{M}$ is an $(m-1)$ -dimensional submanifold. But in general, $\partial\mathcal{M}$ need not be differentiable everywhere (which is a requirement of a manifold). For example, if \mathcal{M} is a triangle in a two-dimensional affine space, then $\partial\mathcal{M}$ is composed of three sides. Each side is a submanifold (with edge): but the union of the three sides does not form a manifold, because it is not differentiable at the vertices

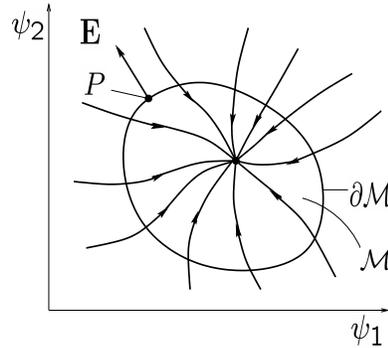


Figure 9. Sketch of a convex, reaction-mapped region \mathcal{M} with edge $\partial\mathcal{M}$, showing the edge vector \mathbf{E} at point P .

where the sides intersect. We restrict our attention to “regular” points on $\partial\mathcal{M}$ at which (by definition) $\partial\mathcal{M}$ is differentiable.

Consider a regular point P on the edge $\partial\mathcal{M}$ of the m -dimensional manifold \mathcal{M} . The tangent space \mathcal{T} of \mathcal{M} at P is m -dimensional, and the normal space \mathcal{N} is $(n_\phi - m)$ -dimensional. For the submanifold $\partial\mathcal{M}$, its tangent space at P , denoted by $\partial\mathcal{T}$ is an $(m - 1)$ -dimensional subspace of \mathcal{T} which we refer to as the *edge-tangent* subspace of \mathcal{M} at P . The orthogonal complement of $\partial\mathcal{T}$ in \mathcal{T} is the one-dimensional *edge-normal* subspace, $\partial\mathcal{T}^\perp$. The *edge vector* \mathbf{E} at P is uniquely defined on the unit vector in $\partial\mathcal{T}^\perp$ which is directed away from \mathcal{M} . With this construction, the n_ϕ -dimensional composition space is spanned by the edge vector \mathbf{E} , the edge-tangent subspace $\partial\mathcal{T}$ and the normal subspace \mathcal{N} , which are mutually orthogonal.

For a point in the interior of \mathcal{M} , motion in the tangent space $\dot{\phi}^\parallel$ causes the composition to remain in \mathcal{M} . But for the point P on the edge $\partial\mathcal{M}$, motion in the edge-normal direction of the tangent space can cause the composition to leave \mathcal{M} , thus increasing the accessed region \mathcal{A} (without increasing its dimension).

An equation describing the motion of compositions in the edge-normal direction is obtained by taking the dot product of Eq.(45) and the edge vector \mathbf{E} . The result can be written

$$\dot{\phi}^E \equiv \mathbf{E} \cdot \left(\frac{D\phi}{Dt} \right) = E_p \Gamma \nabla^2 \theta_p + K_{pq}^E \chi_{pq} + S^E, \quad (59)$$

where $E_p \equiv \mathbf{E} \cdot \mathbf{T}_p$ is the p -th component of \mathbf{E} in the tangent-space basis, K_{pq}^E is the *edge-curvature matrix*

$$K_{pq}^E \equiv \mathbf{E} \cdot \mathbf{K}_{pq}, \quad (60)$$

and

$$S^E \equiv \mathbf{E} \cdot \mathbf{S}, \quad (61)$$

is the component of the reaction vector in the \mathbf{E} direction.

For a given manifold \mathcal{M} with edge $\partial\mathcal{M}$, the edge normal \mathbf{E} at a point P on $\partial\mathcal{M}$ is an intrinsic property, i.e., independent of the parametrization. Hence we can choose a local parametrization at P to simplify the interpretation of Eq.(59). Thus we choose the parametrization $\Phi(\boldsymbol{\eta})$ such that

i) $\partial\mathcal{M}$ is defined by $\eta_1 = 0$

ii) $\eta_1 \geq 0$ in \mathcal{M}

iii) the m tangent vectors $\partial\Phi/\partial\eta_p$ are orthonormal

iv) the parameters $\eta_2, \eta_3, \dots, \eta_m$ are such that the lower right $(m-1) \times (m-1)$ block of the symmetric matrix K_{pq}^E is diagonal, i.e., $K_{pq}^E = 0$ for $p, q \geq 2, p \neq q$.

It follows from (i) and (iii) that $\partial\Phi/\partial\eta_p$ for $p = 2, 3, \dots, m$ provide an orthonormal basis for the edge-tangent space $\partial\mathcal{T}$, and that $\partial\Phi/\partial\eta_1$ spans the edge-normal space. Further, from (i) and (ii) it follows that the edge vector is

$$\mathbf{E} = -\frac{\partial\Phi}{\partial\eta_1}. \quad (62)$$

(Note that, in view of (iii), $|\partial\Phi/\partial\eta_1| = 1$.) It then follows from its definition that E_p is

$$E_p \equiv \mathbf{E} \cdot \mathbf{T}_p = -\delta_{p1}. \quad (63)$$

We now return to examine Eq.(59) using this parametrization. The left-hand side $\dot{\phi}^E$ represents the rate of change of composition (following the fluid) in the \mathbf{E} direction. Thus a positive value corresponds to the composition leaving \mathcal{M} . The final term S^E is the contribution to this rate of change due to reaction. The first term on the right-hand side is

$$E_p \Gamma \nabla^2 \theta_p = -\Gamma \nabla^2 \theta_1, \quad (64)$$

where all quantities are evaluated at $\mathbf{x}_0, t_0, \boldsymbol{\theta}_0$ and Eq.(63) has been used. Now at (\mathbf{x}_0, t_0) , there is a local minimum in the parameter field $\theta_1(\mathbf{x}, t)$ (since $\theta_1(\mathbf{x}_0, t_0) = 0$ and $\theta_1(\mathbf{x}, t) \geq 0$). Thus we have

$$(\nabla\theta_1)_{\mathbf{x}_0, t_0} = 0, \quad (\nabla^2\theta_1)_{\mathbf{x}_0, t_0} \geq 0. \quad (65)$$

Hence we obtain

$$E_p \Gamma \nabla^2 \theta_p \leq 0 : \quad (66)$$

the term cannot cause the composition to leave \mathcal{M} .

The final term to consider is $K_{pq}^E \chi_{pq}$. We first observe that $\chi_{p1} = \chi_{1p} = 0$, because $\nabla\theta_1$ is zero at P (Eq.(65)). Second, the parametrization is chosen such that the lower right $(m-1) \times (m-1)$ block of K_{pq}^E is diagonal. Thus we have

$$K_{pq}^E \chi_{pq} = \sum_{p=2}^m K_{(p)(p)}^E \chi_{(p)(p)}, \quad (67)$$

where bracketed suffixes are excluded from the summation convention. And we observe that $\chi_{(p)(p)}$ is non-negative:

$$\chi_{(p)(p)} = \Gamma |\nabla\theta_{(p)}|^2 \geq 0. \quad (68)$$

For $p \geq 2$ we have

$$K_{(p)(p)}^E = \mathbf{E} \cdot \mathbf{K}_{(p)(p)} = \mathbf{E} \cdot \frac{\partial^2 \Phi}{\partial \eta_{(p)}^2} = \frac{\partial^2 \Phi^E}{\partial \eta_{(p)}^2}, \quad (69)$$

where

$$\Phi^E(\boldsymbol{\eta}) \equiv \mathbf{E} \cdot [\Phi(\boldsymbol{\eta}) - \Phi(\boldsymbol{\theta}_0)] \quad (70)$$

represents the displacement of the manifold (relative to $\Phi(\boldsymbol{\theta}_0)$) in the edge-normal direction. The tangent vectors $\partial\Phi(\boldsymbol{\eta})/\partial\eta_p$ ($p \geq 2$) correspond to the directions of principal curvature of $\partial\mathcal{M}$, and $K_{(p)(p)}^E$ are the $(m-1)$ principal curvatures. Convex and concave curvature correspond to negative and positive values of $K_{(p)(p)}^E$, respectively. Thus the term

$$K_{pq}^E \chi_{pq} = \sum_{p=2}^m K_{(p)(p)}^E \Gamma |\nabla\theta_{(p)}|^2, \quad (71)$$

is non-positive if $\partial\mathcal{M}$ is convex (so that $K_{(p)(p)}^E \leq 0$), and hence cannot cause the composition to leave \mathcal{M} (if $\partial\mathcal{M}$ is convex).

For the case depicted in Fig. 5, in which \mathcal{M} is a convex, reaction-mapped region, compositions cannot leave \mathcal{M} , because each term on the right-hand side of Eq.(59) is non-positive, leading to $\dot{\phi}^E \leq 0$. Conversely, if reaction vectors are outward pointing on $\partial\mathcal{M}$ (i.e., $S^E > 0$), or if $\partial\mathcal{M}$ is concave in one or more directions, then $\dot{\phi}^E$ may be positive, indicating that the composition leaves \mathcal{M} due to reaction or mixing, respectively. However, this is not inevitable, as is now discussed.

Consider the case of inert mixing between three streams A , B and C . As depicted in Fig. 5 (a), the boundary region \mathcal{B} consists of three points ϕ^A , ϕ^B and ϕ^C , and so \mathcal{B}^+ is a triangle in a two-dimensional affine space. Suppose that the flow consists of A and B being introduced at the beginning of a long pipe, with C being injected into the flow

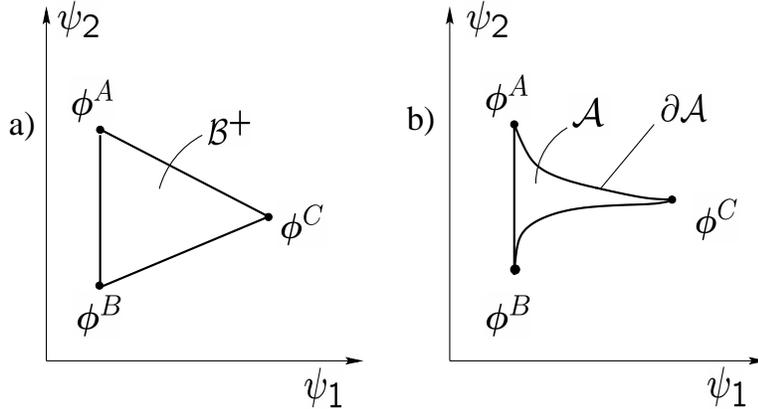


Figure 10. Sketch of (a) the convex hull \mathcal{B}^+ of three compositions ϕ^A , ϕ^B , and ϕ^C , and (b) the accessed region in the case of flow shielding.

some distance downstream. Then the accessed region \mathcal{A} is a non-convex region, such as that depicted in Fig. 5 (b). The lines $\phi^A - \phi^C$ and $\phi^B - \phi^C$ are not in \mathcal{A} because, at the location where stream C is injected, the fluid from streams A and B have mixed with each other to some extent. Because of the geometry of the flow there is no mixing between pure C fluid and pure A or B fluid. We refer to such phenomena which yield a non-convex accessed region as *flow shielding*.

In this situation, part of the edge $\partial\mathcal{M}$ of the accessed region \mathcal{A} is concave ($K_{(p)(p)}^E > 0$), but nevertheless $|\nabla\theta_{(p)}|$ is such that the sum of $K_{(p)(p)}^E |\nabla\theta_{(p)}|^2$ and hence $\dot{\phi}^E$ is non-positive (see Eq.(59) and Eq.(71)). For $m = 2$ (i.e., $m - 1 = 1$) this requires $|\nabla\theta_2| = 0$; while for $m > 2$, a positive contribution to the sum from a concave direction can be counteracted by a larger negative contribution from a convex direction.

A second phenomenon leading to a non-convex accessed region is *strong inward reaction*, as depicted in Fig. 5. At the point P on $\partial\mathcal{M}$, mixing can cause the composition to move out of \mathcal{M} , but in the case considered, the effect of mixing is overpowered by strong inward reaction, i.e., S^E is large and negative.

A third case is that of *weak outward reaction* depicted in Fig. 5, in which \mathcal{M} is not a reaction-mapped region. At the points P and Q on $\partial\mathcal{M}$, the reaction trajectories are outward pointing, ($S^E > 0$) but (for the case considered) $|S^E|$ is relatively small, and reaction is overpowered by strong inward mixing. In the context of combustion, this situation may arise close to equilibrium (illustrated by P in Fig. 5) or in cold, barely-reactive mixtures (illustrated by Q in Fig. 5).

It may be noted that the phenomena of strong inward reaction and weak outward reaction require an upper and lower bound, respectively,

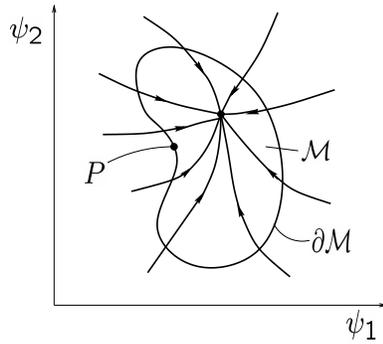


Figure 11. Sketch of a manifold \mathcal{M} with edge $\partial\mathcal{M}$ showing strong inward reaction (at point P on $\partial\mathcal{M}$).

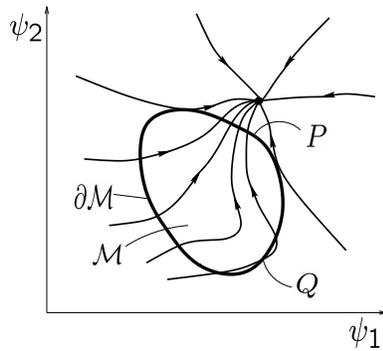


Figure 12. Sketch of a manifold \mathcal{M} with edge $\partial\mathcal{M}$ showing weak outward reaction at points P and Q .

on the rate of change of composition due to mixing. In a turbulent flow, such bounds may be satisfied with high probability, if not with certainty.

6. Summary and Conclusions

We have examined the region \mathcal{A} of the n_ϕ -dimensional composition space \mathcal{C} which is accessed in a reactive flow governed by Eq.(28). This equation includes the strong assumption of equal molecular diffusivities, which is necessary in order to obtain most of the results.

In the absence of information on initial and boundary conditions, all that can be said about \mathcal{A} is that it is contained in the realizable region of \mathcal{C} , which is in an $(n_\phi - 1)$ -dimensional affine space.

If the initial and boundary conditions are contained in an m -dimensional manifold \mathcal{B} in an a -dimensional affine space ($a \geq m$), then:

1. In the absence of reaction ($\mathbf{S} = 0$), the accessed region is the convex hull $\mathcal{B}^+ = \text{hull}(\mathcal{B})$, which is in the same a -dimensional affine space as \mathcal{B} .
2. In the absence of mixing ($\Gamma = 0$), the accessed region is the reaction mapping of \mathcal{B} , $\mathcal{B}_{\mathcal{R}} \equiv \mathcal{R}(\mathcal{B})$ which is contained in an $(m + 1)$ -dimensional manifold.
3. With simultaneous reaction and mixing, the accessed region can be of much greater dimensionality than with either mixing or reaction alone. Specifically, \mathcal{A} is the smallest convex, reaction-mapped region containing \mathcal{B} . It is contained in an affine space of dimension

$$\dim(\mathcal{B}^0 \cup \mathcal{C}'_{\mathcal{R}}),$$

where \mathcal{B}^0 is the tangent space of \mathcal{B}^+ and $\mathcal{C}'_{\mathcal{R}}$ is the accessed reactive subspace.

If the initial and boundary conditions are confined to n_b distinct compositions, then $\mathcal{B}^+ \equiv \text{hull}(\mathcal{B})$ is a convex polytope in an $(n'_b - 1)$ -dimensional affine space, where $n'_b \leq n_b$ is the number of linearly independent compositions in \mathcal{B} .

In general, the accessed region can be considered to be contained in an m -dimensional manifold \mathcal{M} with edge $\partial\mathcal{M}$. Away from the edge, the rate of change of composition can be decomposed into a component in the tangent space, $\dot{\phi}^{\parallel}$, and a component in the normal space, $\dot{\phi}^{\perp}$. A non-zero value of $\dot{\phi}^{\perp}$ corresponds to motion normal to the manifold, and thus to increasing the dimensionality of the accessed region. By examining the equation for $\dot{\phi}^{\perp}$ (see Eq.(46) and Eq.(48)), we have shown that for a curved manifold \mathcal{M} , a necessary condition for $\dot{\phi}^{\perp}$ to be zero is that there be no conditional fluctuations in the mixing. This condition is satisfied for laminar flows, in which the accessed region can indeed be a curved manifold. But in the turbulent case, this condition is not satisfied, and so the accessed region is a plane manifold (or affine space). Nevertheless, in regions on strongly attracting ILDMs, compositions may be very close to a curved manifold.

At the edge $\partial\mathcal{M}$ of the manifold \mathcal{M} , the m -dimensional tangent space can be decomposed into the edge normal vector \mathbf{E} and the $(m-1)$ -dimensional edge-tangent space. If $\dot{\phi}^E \equiv \mathbf{E} \cdot \dot{\phi}$ is positive, then the accessed region is extended beyond \mathcal{M} , but without an increase in dimension. The equation for $\dot{\phi}^E$ Eq.(59) is derived and discussed, and three situations are identified in which the edge of the accessed region may be non-convex or may have outward-pointing reaction vectors.

These are: flow shielding, strong inward reaction, and weak outward reaction.

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