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Description of mixing with diffusion and reaction in terms of the concept of material surfaces

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The essence of fluid-mechanical mixing of diffusing and reacting fluids can be traced back to kinematics, connectedness of material volumes and transport processes occurring across deforming material surfaces. Descriptions based on kinematics of homoeomorphic deforming material surfaces (tracers) are restricted solely to continuous motions and conveniently analysed by transport equations in Lagrangian frames.

Connectedness of material volumes restricts the mixing topology and generates bicontinuous structures characterized by intermaterial-area and striation-thickness distributions. Upper bounds for area generation and material-line elongation are related to mean values of viscous dissipation and govern the average reaction rate in diffusion-controlled reactions. Two concepts are introduced: micromixing, related to local flows, rate of stretching and local viscous dissipation, and macromixing, associated with connectedness of isoconcentration surfaces, vorticity and average viscous dissipation.

Several small-scale flows can be used to typify the interplay between fluid mechanics, mass and energy transport, and chemical reactions: elliptically symmetrical stagnation flows, vortex decay, and swirling flow with uniform stretching. It is proposed that complex fluid motions might be interpreted in terms of integrated behaviour of populations of small-scale flows distributed in space and time to simulate mixing behaviour.

The objective of this work is to present the foundations of a continuum mixing description making reference to earlier approaches to demonstrate computational applicability and practical significance.

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1. Introduction

Turbulent mixing of diffusing and reacting fluids is a process that involves fluid mechanics, mass and energy transport, and chemical reactions. In general, these four mechanisms govern reaction in any reacting mixture and any reasonable mixing description should give an emphasis to all these contributions in proportion to the importance of their effects. Applications of these descriptions are relevant to combustion, chemical reactors, and are a central theme in physico-chemical hydrodynamics.

The present understanding of mixing and methods of simulation is well represented by Brodkey (1975), Murthy (1975) and Hill (1976). Analyses are based fundamentally on the Reynolds, Taylor, von Kármán tradition of the statistical theory of turbulence (e.g. Monin & Yaglom 1971). However, as noted by Marble & Broadwell (1977), some of the earliest considerations on reactive turbulent mixing put forward the suggestion that a seemingly chaotic mixing field might be modelled by a collection of identifiable small-scale reactive surfaces distorted by the turbulent motion (e.g. Damköhler 1940). This conjecture found additional support in the works of Hawthorne (1948), Karlovitz, Denniston & Wells (1951), Hottel (1952), Wohl *et al.* (1952), Yamazaki & Tsuji (1960) and others.

Fluid-mechanical mixing descriptions based on a concept of small-scale laminar reacting elements have not been developed to the level of the statistical descriptions. An eclectic list of works generated by this point of view is: Fisher (1968, 1974), Mao & Toor (1970), Gibson & Libby (1972), Spalding (1976*a–c*, 1978*a, b*), Marble & Broadwell (1977), Ranz (1979*a*), Ottino (1980). However, considerable improvements on the theoretical bases of such analyses are possible; specifically concerning the kinematical structure, description of transport in moving frames of reference, local-flow analyses and relation with experimental information.

Although substantial applications of this approach, involving varying degrees of complexity, have been made (e.g. Spalding 1978*b*; Marble & Broadwell 1977), the theoretical foundations of this point of view are still not clear. It is desirable that further applications should proceed on a firmer theoretical basis.

The objective of the present work is to present a coherent and concise description of this alternative point of view and formulate a mixing theory based on the concept of material surfaces. The paper starts with a continuum description of mixing of multi-component reacting mixtures, kinematics and structures produced by continuous motions and analyses of transport equations in moving frames. A concept of material surface and tracer is introduced to quantify mixing efficiency and linked with local small-scale flows containing the essence of local motion-transport interactions. Parenthetical reference is given throughout the paper to the more practical computational approach offered by Spalding (1978*b*) as well as additional related literature.

2. Background

(*a*) *Kinematical descriptions and mass balances in multi-component mixtures*

The kinematical basis of diffusion lies in the existence of N continuous mappings $\chi_\alpha, \alpha = 1, \ldots, N$, (Bowen 1976) such that

$$\mathbf{x}_\alpha = \chi_\alpha(\mathbf{X}_\alpha, t), \quad \mathbf{X}_\alpha = \chi_\alpha(\mathbf{X}_\alpha, 0), \tag{1}$$

where $\mathbf{X}_\alpha$ represents the configuration position of species α and $\mathbf{x}_\alpha$ its position at the present time t. Each species is assigned a mass density $\rho_\alpha = \rho_\alpha(\mathbf{x}, t)$ such that $\rho = \Sigma_{\alpha=1}^{N} \rho_\alpha$ is the density of the mixture. Individual velocities are defined as

$$\mathbf{v}_\alpha = \left.\frac{\partial \chi_\alpha(\mathbf{X}_\alpha, t)}{\partial t}\right|_{\mathbf{X}_\alpha}, \tag{2}$$

and the average mass velocity as

$$\mathbf{v} = \sum_{\alpha=1}^{N} \frac{\rho_\alpha}{\rho} \mathbf{v}_\alpha. \tag{3}$$

The material derivatives of any function f following the motion of the α-component and the average motion are defined by

$$\frac{D_\alpha f}{Dt} = \frac{\partial f}{\partial t} + \mathbf{v}_\alpha . \nabla f, \tag{4}$$

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \mathbf{v} . \nabla f, \tag{5}$$

respectively. The relative velocities are defined as

$$\mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}. \tag{6}$$

A change of frame between any two frames F and $\bar{F}$ is represented by

$$\bar{\mathbf{x}} = \mathbf{c}(t) + \mathbf{Q}(t) . \mathbf{x}, \tag{7}$$

where $\mathbf{c}(t)$ is any vector and $\mathbf{Q}(t)$ is a time-dependent orthogonal tensor. Overbars indicate quantities in frame $\bar{F}$. Relative velocities $\bar{\mathbf{u}}_\alpha$ and $\mathbf{u}_\alpha$ are related by

$$\bar{\mathbf{u}}_\alpha = \mathbf{Q}(t) . \mathbf{u}_\alpha, \tag{8}$$

and are therefore indifferent.

By a material surface we mean a surface $f(\mathbf{x}, t) = 0$ that moves with the mean velocity (3), and by a *tracer* we mean a hypothetical material that moves everywhere with the mean velocity of the mixture. Since each point of the mixture has a uniquely defined mass velocity, the motion of particles of tracer is properly defined. We conceptualize material lines and surfaces in terms of particles of tracer moving everywhere with the mean mass velocity. Material lines and surfaces do not break or change topology. In particular, material surfaces do not diffuse. They are however, permeable to the diffusion of all other species.

A necessary and sufficient condition for $f(\mathbf{x}, t) = 0$ to be a material surface is

$$\frac{Df}{Dt} = 0. \tag{9}$$

For a material to be a tracer a necessary and sufficient condition is

$$\mathbf{v}_\mathrm{m} - \mathbf{v} = \mathbf{u}_\mathrm{m} = 0, \tag{10}$$

where subscript m refers to the tracer material. The mass-conservation principle for the multi-component reacting mixture is (Bowen 1976, p. 11)

$$\rho \frac{Dw_\alpha}{Dt} = -\nabla . (\rho_\alpha \mathbf{u}_\alpha) + \hat{w}_\alpha, \tag{11}$$

where $w_\alpha = \rho_\alpha / \rho$, and $\hat{w}_\alpha$ represents a homogeneous chemical reaction for component α. A tracer thus satisfies

$$\rho \frac{Dw_\mathrm{m}}{Dt} = \hat{w}_\mathrm{m} \tag{12}$$

and can in principle be a reacting material, but, in order to avoid $w_\mathrm{m} = 0$, $\hat{w}_\mathrm{m}$ is set equal to zero. Under these conditions, isoconcentration surfaces of the tracer are connected material surfaces and describe totally the average mass motion of the reacting mixture. The mass balance of species α (11) is invariant, i.e. its form is unchanged for any two frames F and $\bar{F}$ related by (7). Thus we have

$$\rho = \bar{\rho}, \quad t = \bar{t}, \quad w_\alpha = \bar{w}_\alpha, \quad \hat{w}_\alpha = \bar{\hat{w}}_\alpha, \quad \bar{\mathbf{u}}_\alpha = \mathbf{Q}.\mathbf{u}_\alpha, \quad \bar{\nabla} = \mathbf{Q}.\nabla, \tag{13}$$

$$\bar{\rho}\frac{D\bar{w}_\alpha}{Dt} = -\bar{\nabla}.(\bar{\rho}_\alpha \bar{\mathbf{u}}_\alpha) + \bar{\hat{w}}_\alpha \quad \text{in } \bar{F}. \tag{14}$$

For simplicity, overbars will be omitted in subsequent sections. The classical theory of diffusion (usually $N = 2$) is based on a phenomenological relation

$$\rho_\alpha \mathbf{u}_\alpha = D\nabla w_\alpha, \tag{15}$$

where D is the Fickean diffusion coefficient and $\rho_\alpha \mathbf{u}_\alpha$ is the mass flux vector. For a multi-component mixture of dilute uncharged materials of nearly constant density, and neglecting all diffusion other than ordinary diffusion (Bird, Stewart & Lightfoot 1960, p. 557), (14) reduces to

$$\frac{D\rho_\alpha}{Dt} = D_\alpha \nabla^2 \rho_\alpha + \hat{\rho}_\alpha, \tag{16}$$

where the D_α are to be interpreted as effective diffusion coefficients. Since the Fickean postulate (15) is invariant (cf. (13)), (16) is also invariant.† The same equation holds in any moving frame. A similar transport equation is satisfied for energy transfer; i.e. the temperature field satisfies

$$\frac{DT}{Dt} = \alpha \nabla^2 T + r, \tag{17}$$

where α is an average thermal diffusivity and r is a generation term that includes energy due to chemical reaction, viscous dissipation, and volume change (cf. Bird *et al.* 1960, p. 562). In general, (16) and (17) are coupled through temperature-dependent kinetic coefficients. (A special case corresponds to the so-called unit-Lewis-number assumption under which (16) and (17) can be reduced to a single partial differential equation; see, e.g., Spalding (1978*b*).)

(*b*) *Mixing in lamellar structures*

The assumption of continuous motions (1) implies connectedness of initially designated material surfaces and hence conservation of topological features. Initially designated material surfaces of a tracer remain connected in time during fluid-mechanical mixing. Sectioning at an instant of time will reveal a lamellar marbled structure (Ranz 1979*a*). It should be noted that, if the initially defined material surface is finite, discontinuous structures might arise. (The lamellar-structure assumption is confirmed in principle by high-speed photography in turbulent shear flows (Roshko 1975). It is noted that Roshko's flow visualization is a shadowgraph which integrates along the span of the flow and not a proper two-dimensional cut. It is believed that a cross-sectional cut would have displaced a lamellar marbled structure. A similar indication is found

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† Frame indifference of mass balances is usually assumed, although Lagrangian descriptions based on (14) and (16) involving a local flow field are sometimes in error. See the discussion following (66).

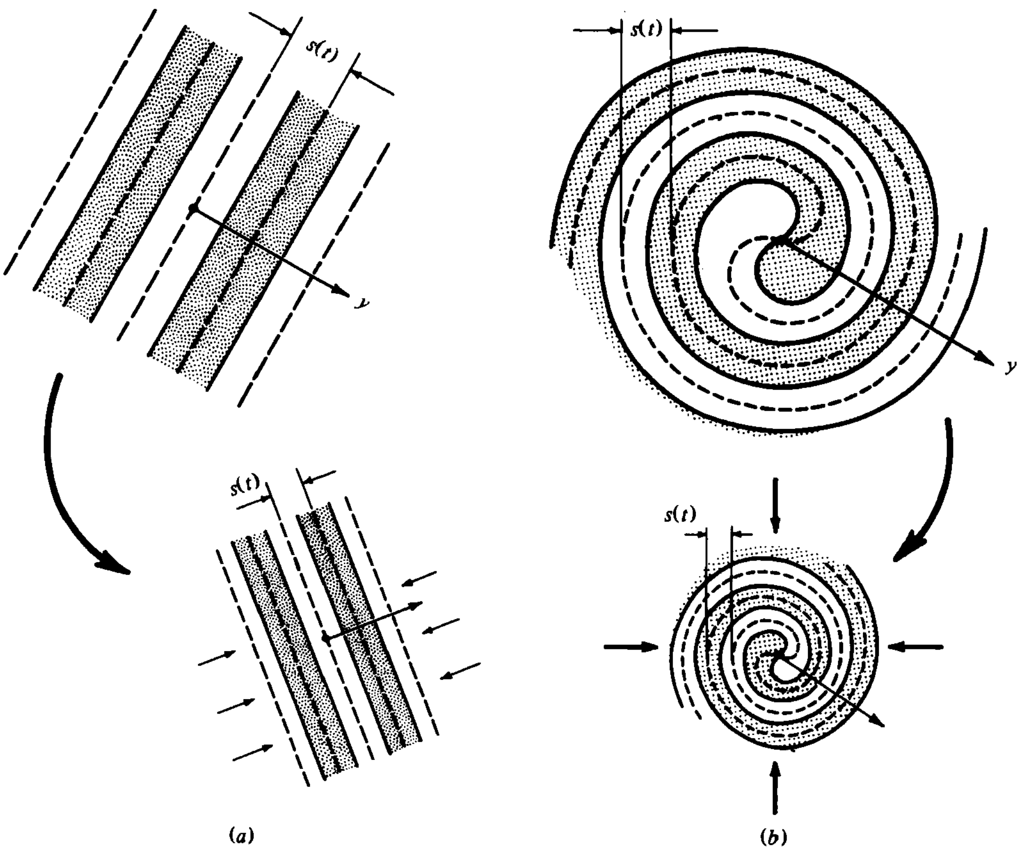

FIGURE 1. Examples of lamellar structures. Dotted lines represent isoconcentration surfaces. $s(t)$ represents an instantaneous striation thickness which is changing owing to a local flow.

in high-speed motion pictures showing the rolling up of a vortex sheet between two reading streams A and B to form a product C of a different colour (A. Roshko, Seminar presented at the Dept of Aerospace and Mechanics, University of Minnesota, 6 April 1979).

Consider a material point in the reacting multi-component mixture with an associated unit vector $\hat{\mathbf{n}}$ and a local orthogonal frame $\bar{F}(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ defined by

$$\mathbf{e}_1 = \hat{\mathbf{n}}; \quad \mathbf{e}_1 . \mathbf{e}_2 = 0, \quad \mathbf{e}_2 . \mathbf{e}_3 = 0, \quad \mathbf{e}_1 . \mathbf{e}_3 = 0. \tag{18}$$

The lamellar-structure hypothesis states that for any fluid-mechanical mixing and any point in the mixture it is possible to define a local frame such that

$$\nabla w_\alpha = (\partial w_\alpha / \partial y, 0, 0) \quad \text{in} \quad \bar{F}, \tag{19}$$

where y is a co-ordinate in direction $\mathbf{e}_1$ which is normal to material planes in a planar lamellar structure (figure 1*a*) or a radial direction in a vortical flow (figure 16). The term $\partial w_\alpha / \partial y$ is assumed to be a quasi-periodic function of distance y. The period (wavelength) specifies a characteristic length scale called the striation thickness s. Figure 1 shows examples of two-dimensional cuts of three-dimensional lamellar structures.

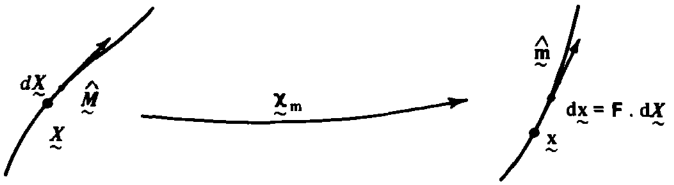

FIGURE 2. Stretching of a differential material filament at X_m.

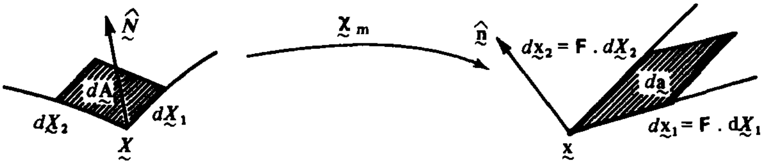

FIGURE 3. Stretching of a differential material plane at X_m.

The assumption of lamellar topology and quasi-periodic structure implies the periodicity condition $\partial w_a/\partial y = 0$ on concentration fields. This boundary or symmetry condition for (16) is used by Spalding (1978*b*) under the claim of non-communication of folds. Some discussion on non-communication and striation-thickness distribution is given by Ottino (1980).

(*c*) *Kinematics of material elements*

The kinematics of material (tracer) elements is represented by the motion

$$\mathbf{x}_m = \chi_m(\mathbf{X}_m, t), \quad \mathbf{X}_m = \chi_m(\mathbf{X}_m, 0), \tag{20}$$

which describes the transformation of particles $\mathbf{X}_m$ at time $t = 0$ to position $\mathbf{x}_m$ at time t. The non-singular deformation gradient $\mathbf{F}_m(\mathbf{X}_m, t)$ and the velocity gradient $\mathbf{L}_m(\mathbf{X}_m, t)$ associated with the motion χ_m are defined respectively by

$$\mathbf{F}_m = [F_{mij}] = \frac{\partial x_{mj}}{\partial X_{mi}}, \quad \mathbf{L}_m = [L_{mij}] = \frac{\partial v_{mj}}{\partial x_i}. \tag{21}$$

The mechanical component of mixing is considered as a deformation and is computed as linear stretch and area stretch of material elements. Thus the linear stretch λ of an initial differential material filament at $\mathbf{X}_m$ (figure 2) of length $|d\mathbf{X}_m|$ and orientation $\hat{\mathbf{M}}$ to a point $\mathbf{x}_m$ at the present time t with length $|d\mathbf{x}_m|$ and orientation $\hat{\mathbf{m}}$ is given by

$$\lambda \equiv |d\mathbf{x}_m|/|d\mathbf{X}_m|. \tag{22}$$

Linear stretch λ, and orientation $\hat{\mathbf{m}}$ are related to the motion by

$$\lambda = (\mathbf{C}_m : \hat{\mathbf{M}}\hat{\mathbf{M}})^{\frac{1}{2}}, \quad \mathbf{C}_m = \mathbf{F}_m^T . \mathbf{F}_m, \tag{23}$$

$$\hat{\mathbf{m}} = \frac{\mathbf{F}_m . \hat{\mathbf{M}}}{\lambda}. \tag{24}$$

The area stretch η of an initial infinitesimal material surface at $\mathbf{X}_m$ (figure 3) of initial area $|d\mathbf{A}|$ and orientation $\hat{\mathbf{N}}$ to a point $\mathbf{x}_m$ at the present time t with area $|d\mathbf{a}|$ and orientation $\hat{\mathbf{n}}$ is given by

$$\eta \equiv |d\mathbf{a}|/|d\mathbf{A}|. \tag{25}$$

Area stretch η and orientation $\hat{\mathbf{n}}$ are related to the motion by

$$\eta \equiv ((\det \mathbf{F}_m)^2 \mathbf{C}_m^{-1} : \hat{\mathbf{N}}\hat{\mathbf{N}})^{\frac{1}{2}}, \tag{26}$$

$$\hat{\mathbf{n}} = \frac{(\det \mathbf{F}_m)^2 (\mathbf{F}_m^{-1}).\hat{\mathbf{N}}}{\lambda}. \tag{27}$$

The length of a material line defined by the set of orientations $\{\hat{\mathbf{M}}\}$ is given by

$$L(\{\hat{\mathbf{M}}\}, t) = \int_{\mathscr{L}_0} (\mathbf{C}_m : \hat{\mathbf{M}}\hat{\mathbf{M}})^{\frac{1}{2}} \, |d\mathbf{X}_m|, \tag{28}$$

whereas the area of a material surface defined by the set of orientations $\{\hat{\mathbf{N}}\}$ is given by

$$A(\{\hat{\mathbf{N}}\}, t) = \int_{\mathscr{S}_0} ((\det \mathbf{F}_m)^2 \mathbf{C}_m^{-1} : \hat{\mathbf{N}}\hat{\mathbf{N}})^{\frac{1}{2}} \, |d\mathbf{A}|. \tag{29}$$

$\mathscr{L}_0$ and $\mathscr{S}_0$ denote the region of integration in terms of the reference co-ordinates $\mathbf{X}_m$. Bounds for (28) and (29) are given by the Cauchy–Schwarz inequality as

$$L(\{\hat{\mathbf{M}}\}, t) \leqslant \int_{\mathscr{L}_0} (\mathbf{C}_m : \mathbf{C}_m)^{\frac{1}{2}} \, |d\mathbf{X}_m|, \tag{28a}$$

$$A(\{\hat{\mathbf{M}}\}, t) \leqslant \int_{\mathscr{S}_0} (\det \mathbf{F}_m) (\mathbf{C}_m^{-1} : \mathbf{C}_m^{-1})^{\frac{1}{2}} \, |d\mathbf{A}|. \tag{29a}$$

The material time rate of change of linear and area stretch per unit of present linear and area stretch are given respectively by (cf. Batchelor 1967, p. 132; Ottino, Ranz & Macosko 1979)

$$\frac{1}{\lambda}\frac{D\lambda}{Dt} = \mathbf{D} : \hat{\mathbf{m}}\hat{\mathbf{m}}, \tag{30}$$

$$\frac{1}{\eta}\frac{D\eta}{Dt} = \nabla . \mathbf{v} - \mathbf{D} : \hat{\mathbf{n}}\hat{\mathbf{n}}, \tag{31}$$

where $\mathbf{v}_m = \mathbf{v}$ has been used (hence the usefulness of a tracer). Alternative formulas appropriate for compressible fluids are

$$\frac{1}{\rho\eta}\frac{D}{Dt}(\rho\eta) = -\mathbf{D} : \hat{\mathbf{n}}\hat{\mathbf{n}}, \tag{31a}$$

$$\frac{1}{\eta}\frac{D\eta}{Dt} = -\left(\frac{1}{\rho}\frac{D\rho}{Dt} + \mathbf{D} : \hat{\mathbf{n}}\hat{\mathbf{n}}\right). \tag{31b}$$

The upper bound of (30) and (31) is given by the Cauchy–Schwarz inequality

$$\frac{1}{\lambda}\frac{D\lambda}{Dt} \leqslant |(\mathbf{D} : \mathbf{D})^{\frac{1}{2}}|, \tag{32}$$

$$\frac{1}{\eta}\frac{D\eta}{Dt} \leqslant \nabla . \mathbf{v} + |(\mathbf{D} : \mathbf{D})^{\frac{1}{2}}|. \tag{33}$$

$\mathbf{D} = \frac{1}{2}(\mathbf{L}+\mathbf{L}^T)$ is the stretching tensor such that $\mathbf{L} = \mathbf{D}+\mathbf{\Omega}$, where $\mathbf{\Omega} = \frac{1}{2}(\mathbf{L}-\mathbf{L}^T)$ is the vorticity tensor. For Newtonian mixtures with viscosity μ

$$\frac{1}{\lambda}\frac{D\lambda}{Dt} \leqslant \left(\frac{\epsilon}{2\mu}\right)^{\frac{1}{2}}, \tag{34}$$

$$\frac{1}{\rho\eta}\frac{D(\rho\eta)}{Dt} \leqslant \left(\frac{\epsilon}{2\mu}\right)^{\frac{1}{2}}, \tag{35}$$

where $\epsilon = 2\mu\mathbf{D}:\mathbf{D}$ is the viscous dissipation per unit volume per unit time. Equations (34) and (35) can be written as

$$\frac{1}{\lambda}\frac{D\lambda}{Dt} = e_\lambda(\mathbf{X}_{\mathrm{m}},t)\left(\frac{\epsilon}{2\mu}\right)^{\frac{1}{2}}, \tag{36}$$

$$\frac{1}{\rho\eta}\frac{D(\rho\eta)}{Dt} = e_\eta(\mathbf{X}_{\mathrm{m}},t)\left(\frac{\epsilon}{2\mu}\right)^{\frac{1}{2}}. \tag{37}$$

Combination of (34), (36) and (35), (37) defines a frame-independent mixing efficiency $e_\lambda \equiv (\mathbf{D}:\hat{\mathbf{m}}\hat{\mathbf{m}})/(\mathbf{D}:\mathbf{D})^{\frac{1}{2}}$, such that $e_\lambda < 1$. Note that e_λ and e_η have a physical meaning of a practical kind and their numerical value provides a measure of the effectiveness of mixing flows. Efficiency can be interpreted as a ratio of energy used to create area or length to energy dissipated by viscous action. According to this definition elongational flows are more effective than shear flows (Ottino 1979). *A given flow can be efficient or inefficient depending on how materials are fed into the flow.*

The necessity of reorientation of material elements to improve mixing efficiency is demonstrated clearly by the difference in local rotational speed of vectors normal to material lines and interfaces and the directions of maximum stretching of the stretching tensor $\mathbf{D}$, $\hat{\mathbf{d}}_i$ (i.e. $\mathbf{D}.\hat{\mathbf{d}}_i = \mathrm{c}_i\,\hat{\mathbf{d}}_i$, corresponding to maximum stretching rate $\lambda^{-1}D\lambda/Dt$ or $(\rho\eta)^{-1}D(\rho\eta)/Dt$. Thus we have

$$\frac{D\hat{\mathbf{m}}}{Dt} = (\mathbf{D}+\mathbf{\Omega}).\hat{\mathbf{m}} - (\mathbf{D}:\hat{\mathbf{m}}\hat{\mathbf{m}})\,\hat{\mathbf{m}}, \tag{38}$$

$$\frac{D\hat{\mathbf{d}}_i}{Dt} = \mathbf{\Omega}.\hat{\mathbf{d}}_i. \tag{39}$$

Lack of correlation between $\hat{\mathbf{m}}$ and $\hat{\mathbf{d}}_i$ implies low mixing efficiency. Mechanically effective mixing flows are those for which $\hat{\mathbf{m}}.\hat{\mathbf{d}}_i$ is a constant or a periodic function with a non-zero average value. This concept is related to the vortical/non-vortical character of the local flow and is discussed in § 2 (*e*).

(*d*) *Description of mixing in terms of intermaterial area per unit volume*

The concept of tracer can be exploited to compute average mechanical mixing. A property called intermaterial area density a_{V} is defined to quantify the state of a system mixed or being mixed. Earlier descriptions of mixing in terms of a_{V} can be found in Ranz (1979*a*) and Ottino *et al.* (1979).

Consider a material surface composed of particles of tracer which at $t = 0$ coincides with the boundary between reactants. As mixing proceeds, and interdiffusion occurs, the material surface moves with the mean mass velocity and is warped by the turbulent motion and finely distributed throughout space. The normal distance between points of the surface quantifies the closeness of the reactants and governs the average reaction rate.

We define $\rho^*(\mathbf{x}, t)$ as the mass of tracer per unit volume for the particle which is at $\mathbf{x}$ at time t. Obviously $\rho^* = 0$ for points $\mathbf{x}$ not belonging to the material surface. If $\mathbf{X}$ is the location at $t = 0$, $\rho^*(\mathbf{X}, 0) = \rho_0^*(\mathbf{X})$ is the reference volume density. It follows that

$$\frac{D}{Dt}\int_V \rho^* \, dV = 0 \tag{40}$$

for any material volume V, and

$$\frac{D\rho^*}{Dt} + \rho^* \nabla . \mathbf{v} = 0. \tag{41}$$

We define $\rho^{\mathrm{n}}(\mathbf{x}, t)$ as the mass of tracer per unit area of material surface for the particle which is at $\mathbf{x}$ and time t on an oriented surface whose normal is $\hat{\mathbf{n}}(\mathbf{x}, t)$. If $\mathbf{X}$ is the position at $t = 0$, $\rho^{\mathrm{n}}(\mathbf{X}, 0) = \rho^{\mathrm{N}}(\mathbf{X})$ is the reference surface density, whereas $\hat{\mathbf{n}}(\mathbf{X}, 0) = \hat{\mathbf{N}}(\mathbf{X})$ is the initial field of orientations. It follows that

$$\frac{D}{Dt}\int_S \rho^{\mathrm{n}} \, da = 0 \tag{42}$$

for any material surface S and in consequence

$$\frac{D\rho^{\mathrm{n}}}{Dt} + \rho^{\mathrm{n}}(\nabla . \mathbf{v} - \mathbf{D} : \hat{\mathbf{n}}\hat{\mathbf{n}}) = 0. \tag{43}$$

Define $a_{\mathrm{V}}(\mathbf{x}, t)$ as $a_{\mathrm{V}} = \rho^*/\rho^{\mathrm{n}}$ and $a_{\mathrm{V}}^0(\mathbf{X})$ as $a_{\mathrm{V}}^0 = \rho_0^*/\rho^{\mathrm{N}}$. It follows that

$$a_{\mathrm{V}} = a_{\mathrm{V}}^0 \eta / \det \mathbf{F}, \tag{44}$$

$$\frac{Da_{\mathrm{V}}}{Dt} + a_{\mathrm{V}} \, \mathbf{D} : \hat{\mathbf{n}}\hat{\mathbf{n}} = 0. \tag{45}$$

The quantity a_{V} is interpreted as area of tracer/volume of fluid and is assumed to be a smooth function of space and time. An equivalent measure of state of mechanical mixing, striation thickness s, is defined as

$$s \equiv 1/a_{\mathrm{V}}. \tag{46}$$

Large values of a_{V} (i.e. small values of s) are to be interpreted to mean good mechanical mixing. In general both a_{V} and s will have spatially distributed values† which might have a large influence on the transport processes occurring in the moving fluids. Consider now the mean values of a_{V}. Formulas are developed for two systems of engineering interest: closed constant-volume systems (e.g. stirred tanks) and continuous-flow systems (e.g. pipe flow, tubular reactors). Representations of these systems are shown in figures 4 (a, b), respectively.

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† Distribution in a_{V} values is likely to affect the reaction at long times. The effects of distributed a_{V} values are described qualitatively by Ottino (1980) and analysed by means of convexity arguments. A distribution of a_{V} values is responsible for diffusional phenomena at scales larger than the s scale.

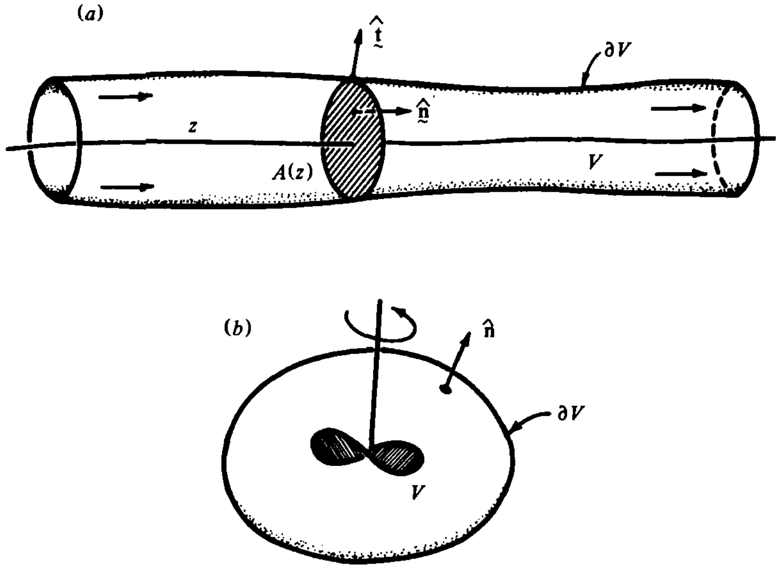

FIGURE 4. (a) Continuous flow system. (b) Closed-volume system.

For systems of constant volume, integration of (45) over volume V (figure 4) leads to

$$\frac{D}{Dt}\overline{\overline{\ln a_V}} = \overline{\overline{e(\mathbf{D}:\mathbf{D})^{\frac{1}{2}}}}, \tag{47}$$

where the mean value of any function $f(\mathbf{x}, t)$ is defined by

$$\bar{\bar{f}} = \frac{\int_V f\,dV}{\int_V dV} \tag{48}$$

on a material volume V.

Equation (47) is proved by using the relation valid for incompressible fluids:

$$\frac{D}{Dt}\int_V \ln a_V\,dV = \int_V \frac{D}{Dt}(\ln a_V)\,dV \tag{49}$$

(Serrin 1960, p. 133).

Equation (45) is now integrated for a general flow system such as the one represented in figure 4 (b). We require the normal velocity component of the velocity $\mathbf{v}$ to the boundary ∂V be zero, i.e.

$$\mathbf{v}|_{\partial V} \cdot \hat{\mathbf{t}} = 0,$$

a condition satisfied by most tubular reactors. We define a gradient operation ∇_A over the cross-sectional areas, such that

$$\nabla(\ \ ) = \nabla_A(\ \ ) + \frac{\partial(\ \ )}{\partial n}\hat{\mathbf{n}},$$

where $\hat{\mathbf{n}}$ is a vector perpendicular to A. Equation (45) is rewritten as

$$\frac{\partial \ln a_{\mathrm{V}}}{\partial t} + \mathbf{v} . \nabla_{\mathrm{A}} \ln a_{\mathrm{V}} + v_{\mathrm{n}} \frac{\partial \ln a_{\mathrm{V}}}{\partial n} = e(\mathbf{D}:\mathbf{D})^{\frac{1}{2}}. \tag{50}$$

For steady flows of incompressible fluid, (46) reduces to

$$\nabla_{\mathrm{A}} . (\mathbf{v} \ln a_{\mathrm{V}}) + \frac{\partial}{\partial n}(\mathrm{v}_{\mathrm{n}} \ln a_{\mathrm{V}}) = e(\mathbf{D}:\mathbf{D})^{\frac{1}{2}}, \tag{51}$$

since

$$\mathbf{v} . \nabla_{\mathrm{A}} \ln a_{\mathrm{V}} = \nabla_{\mathrm{A}} . (\mathbf{v} \ln a_{\mathrm{V}}) - (\nabla_{\mathrm{A}} . \mathbf{v}) \ln a_{\mathrm{V}}, \quad \nabla_{\mathrm{A}} . \mathbf{v} = \frac{-\partial \mathbf{v}_{\mathrm{n}}}{\partial n},$$

$$\int_{\mathrm{A}} \nabla_{\mathrm{A}} . (\mathbf{v} \ln a_{\mathrm{V}}) \, dA = 0 \quad \text{by the condition} \quad \mathbf{v}|_{\partial V} . \hat{\mathbf{t}} = 0.$$

Integration of (51) over the cross-sectional area yields

$$\frac{d}{dn} \int_{\mathrm{A}} v_{\mathrm{n}} \ln a_{\mathrm{V}} \, dA = \int_{\mathrm{A}} e(\mathbf{D}:\mathbf{D})^{\frac{1}{2}} \, dA, \tag{52}$$

$$\frac{d}{dn} \langle\langle \ln a_{\mathrm{V}} \rangle\rangle = \frac{\overline{e(\mathbf{D}:\mathbf{D})^{\frac{1}{2}}}}{\bar{v}_{\mathrm{n}}}, \tag{53}$$

where mean values of any function f are defined by

$$\langle\langle f \rangle\rangle = \frac{\int_{\mathrm{A}} f v_{\mathrm{n}} \, dA}{\int_{\mathrm{A}} v_{\mathrm{n}} \, dA}, \quad \bar{f} = \frac{\int_{\mathrm{A}} f \, dA}{\int_{\mathrm{A}} dA}. \tag{54}$$

In terms of a curvilinear co-ordinate z, everywhere tangent to the vectors $\hat{\mathbf{n}}$ (i.e. there exists a 1–1 correspondence between $\hat{\mathbf{n}}$ and z) we obtain

$$\frac{d}{dz} \langle\langle \ln a_{\mathrm{V}} \rangle\rangle = \frac{\overline{e(\mathbf{D}:\mathbf{D})^{\frac{1}{2}}}}{\bar{v}_z}. \tag{55}$$

Equations for the moments of a_{V} can also be developed. Maximum production of intermaterial area is given by

$$\frac{D}{Dt} \overline{\overline{\ln a_{\mathrm{V}}}} \leqslant \overline{\overline{(\mathbf{D}:\mathbf{D})^{\frac{1}{2}}}} \quad \text{for constant-volume systems,} \tag{56}$$

$$\frac{d}{dz} \langle\langle \ln a_{\mathrm{V}} \rangle\rangle \leqslant \frac{\overline{(\mathbf{D}:\mathbf{D})^{\frac{1}{2}}}}{\bar{v}_z} \quad \text{for continuous-flow systems,} \tag{57}$$

since $e \leqslant 1$. More practical forms of (56), (57) are

$$\frac{D}{Dt} \overline{\overline{\ln a_{\mathrm{V}}}} \leqslant (\overline{\overline{\mathbf{D}:\mathbf{D}}})^{\frac{1}{2}}, \tag{58}$$

$$\frac{d}{dz} \langle\langle \ln a_{\mathrm{V}} \rangle\rangle \leqslant \frac{\overline{(\mathbf{D}:\mathbf{D})}^{\frac{1}{2}}}{\bar{v}_z}, \tag{59}$$

which are obtained by application of the Hölder inequality (Hardy, Littlewood & Pólya 1973).

The right-hand sides of these inequalities are relatively easy to calculate in a known flow field and represent limits to the mixing capacity of macroscopic systems in an average sense. They are also related simply to $\boldsymbol{\tau} : \mathbf{D}$ for some constitutive equations. Values $\overline{\overline{\boldsymbol{\tau} : \mathbf{D}}}$ and $\overline{\boldsymbol{\tau} : \mathbf{D}}$ can be obtained from macroscopic energy balances or experimental measurements of pressure drops or energy input. Equations (58), (59) represent an average mixing description in terms of macroscopic parameters.

3. Transport processes and small-scale flows

According to the description given here, mixing with diffusion and reaction is interpreted in terms of diffusional processes in small-scale flows with kinematics specified by the deformation of material surfaces. This section considers transport in lamellar structures and typical small-scale flows.

(*a*) *Transport processes in lamellar structures*

The assumption of lamellar structure (19) implies that transport equations (16), (17) are written locally as

$$\frac{\partial \rho_\alpha}{\partial t} + v_y \frac{\partial \rho_\alpha}{\partial y} = D \frac{\partial^2 \rho_\alpha}{\partial y^2} + \hat{\rho}_\alpha, \tag{60}$$

$$\frac{\partial \rho_\alpha}{\partial t} + v_y \frac{\partial \rho_\alpha}{\partial y} = \frac{D}{y} \frac{\partial}{\partial y}\left(y \frac{\partial \rho_\alpha}{\partial y}\right) + \hat{\rho}_\alpha \tag{61}$$

in the frame $\bar{F}$ for the lamellar structures of figure 1. In this case the velocity v_y measures the rate of stretching or contraction normal to material interfaces and according to (18), (30), (34)

$$v_y = (\mathbf{D} : \mathbf{e}_1 \mathbf{e}_1) y \leqslant \left(\frac{\epsilon}{2\mu}\right)^{\frac{1}{2}} y. \tag{62}$$

Equations (60), (61) are conveniently transformed in terms of (see appendix)

$$\xi \equiv \frac{y}{s}, \quad \frac{dt}{d\tau} = \frac{s^2(t)}{D} \tag*{(63), (64)}$$

to

$$\frac{\partial \rho_\alpha}{\partial \tau} = \frac{\partial^2 \rho_\alpha}{\partial \xi^2} + \left(\frac{dt}{d\tau}\right) \hat{\rho}_\alpha, \tag{65}$$

$$\frac{\partial \rho_\alpha}{\partial \tau} = \frac{1}{\xi} \frac{\partial}{\partial \xi}\left(\xi \frac{\partial \rho_\alpha}{\partial \xi}\right) + \left(\frac{dt}{d\tau}\right) \hat{\rho}_\alpha, \tag{66}$$

which describe transport on a non-deforming space ξ and warped time τ with an apparent reaction rate increased by $dt/d\tau$. Equations (65), (66) represent the local interaction of motion and mass or heat transport.† Overall transport processes are given by the integrated behaviour of (65), (66).

† Transport equations in moving (Lagrangian) frames involve a local flow field as given by (14) which can also be expressed by approximations such as (67). A careful discussion of this point is given by Chan & Scriven (1970) and is also analysed by Ottino (1980) and Ranz (1979*a*). Local flow-field effects are sometimes incorporated as domain changes in a non-convective diffusion equation (Sperb 1979). This point of view does not, however, correspond to physical reality.

(*b*) *Typified mixing flows*

The smallest-scale flow representations of complex flow fields are kinematically restricted elliptically symmetrical stagnation flows. Thus the expansion of a flow in the frame $\bar{F}'$ centred on the material particle $\mathbf{X}_\mathrm{m}$ at distance $\bar{\mathbf{x}}$ is

$$\bar{\mathbf{v}} \simeq \bar{\mathbf{x}} \,.\, (\overline{\nabla \mathbf{v}})_{\mathbf{X}_\mathrm{m}}. \tag{67}$$

If $\bar{F}'$ is such that its axes are the axes of principal stretching we have

$$(\overline{\nabla \mathbf{v}})_{ij} = \begin{bmatrix} D_{11} & 0 & 0 \\ 0 & D_{22} & 0 \\ 0 & 0 & D_{33} \end{bmatrix}, \tag{68}$$

so the motion around $\mathbf{X}_\mathrm{m}$ is

$$v_i \simeq D_{ii}(\mathbf{X}_\mathrm{m}, t)\, x_i, \tag{69}$$

with $D_{11}+D_{22}+D_{33} = \nabla . \mathbf{v}$ and local dissipation $\epsilon = 2\mu(D_{11}^2+D_{22}^2+D_{33}^2)$. Within this small-scale flow a small material plane remains planar and initially parallel planes remain parallel but come closer together (discussion concerning these flows can be found in Ottino *et al.* (1979)).

Analyses based on local stagnation flows[†] cannot explain distributed values of mixedness. The essence of striation-thickness distribution seems to be closely related to the concept of streamline redistribution (Shearer 1973) and helical or rotational flows (L. E. Scriven, personal communication). Local and volume values of the upper bound of stretching are related to rotation and acceleration. Thus, according to the Bobyleff–Forsythe formula (Serrin 1960, p. 215) the upper bound of stretching can be written as

$$\mathbf{D} : \mathbf{D} = \nabla . \mathbf{a} + \tfrac{1}{2}\boldsymbol{\omega}^2, \tag{70}$$

showing the interplay between acceleration $\mathbf{a}$ and the square of vorticity, $\boldsymbol{\omega}^2$. Stagnation flows produce stretching owing to accelerational components and shear flows owing to rotation. The long-time values of efficiency of these flows are constant and t^{-1}, respectively.

To understand the importance of vorticity in small-scale mixing flows we will consider two simple local flows: vortex decay and axially symmetric swirling flow with uniform stretching. The former is important because of the non-steady character and decaying values of local viscous dissipation, while the latter is particularly significant because it is precisely the local steady state which is approached locally in many turbulent situations.

[†] Analyses of local flows are not common in literature discussing mixing from a Lagrangian point of view, for most of the approaches have considered linear velocity profiles. More detailed flow fields can eventually account for existence of hot spots and thermal explosions. Mixing distributions cannot be created by linear, extensional velocity fields. Mixing distributions are discussed by Ottino (1980).

(c) *Stretching during vortex decay*

Here we consider the case in which vorticity is concentrated on a material axis at $r = 0$ where there is a line vortex of strength C. Initially the constancy of circulation implies $v_\theta = C/2\pi r$ and subsequent times show a vorticity decay (Batchelor 1967, p. 204)

$$\omega(r,t) = \frac{C}{4\pi\nu t}\exp\left(-\frac{r^2}{4\nu t}\right), \tag{71}$$

with a velocity distribution

$$v_r = \frac{C}{2\pi r}\left(1-\exp\left(-\frac{r^2}{4\nu t}\right)\right). \tag{72}$$

At small values of r ($\ll (4\nu t)^{\frac{1}{2}}$) the motion is a rigid-body rotation and is equal to the axially symmetric flow (§ 3 (*d*)) for $t = 1/a$ if $C = 4\pi\nu\omega_0/a$. The length of a material line (or area of a material surface of unit width) with initial length L_0 and oriented initially in the radial direction is

$$L(t) = \int_0^{L_0}\left\{1+r^2\left(\frac{Ct}{\pi r^3}\right)^2\left[1+\left(1+\frac{r^2}{4\nu t}\right)\exp\left(-\frac{r^2}{4\nu t}\right)\right]^2\right\}^{\frac{1}{2}} dr, \tag{73}$$

and shows that $L(t) \simeq t$ for $t \to \infty$ as in simple shear flows (Ottino 1979). The viscous dissipation over the volume of the flow is given only by vorticity contributions (see (70)) since

$$\nabla.\mathbf{a} = \frac{1}{r}\frac{\partial}{\partial r}\left(-\frac{v_\theta^2}{r}r\right), \tag{74}$$

$$\lim_{V\to\infty}\int_V \nabla.\mathbf{a}\,dV = 0. \tag{75}$$

The viscous-dissipation decay is given by

$$\lim_{V\to\infty}\int_V \epsilon\,dV = \mu\int_V \boldsymbol{\omega}^2 dV = \frac{C^2\rho L^0}{8\pi t}, \tag{76}$$

where L^0 is the length of the vortex, and the efficiency of mixing is then given by

$$e = \frac{\dfrac{1}{L(t)}\dfrac{dL(t)}{dt}}{\left(\dfrac{1}{2\mu V}\displaystyle\int_V \epsilon\,dV\right)^{\frac{1}{2}}} \to \frac{1}{t^{\frac{1}{2}}}. \tag{77}$$

Vortex-decay flows are mechanically more effective than shear flows but less effective than elongational flows.

A similar flow is

$$v_\theta = \frac{C_1}{2\pi}\frac{r}{r_1^2} \quad (r \leqslant r_1), \tag{78}$$

$$v_\theta = \frac{C_1}{2\pi r} \quad (r > r_1). \tag{79}$$

The striation-thickness distribution associated with this flow at time t is (Ranz 1979*b*, figure 5)

$$s \simeq \frac{\pi r}{\left(1+\dfrac{C^2t^2}{4\pi r^4}\right)^{\frac{1}{2}}}. \tag{80}$$

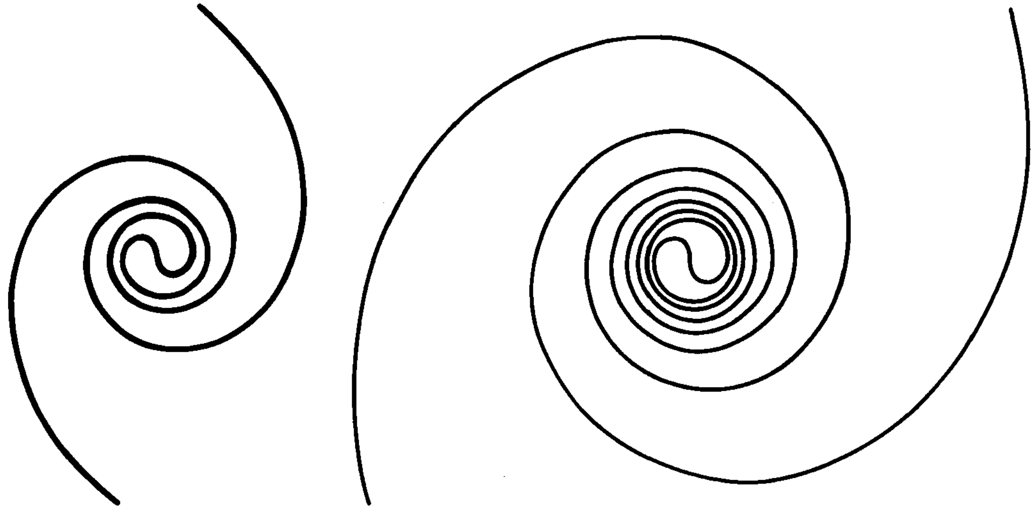

FIGURE 5. Stretching of a material line in a vortex with core (equations (73), (74)) after two and four turns, respectively.

The striation-thickness distribution is $s \simeq r^3$ at a fixed time ($r \gg r_1$ and $s^{-1}\,ds/dt \simeq -1/t$ for $C^2t^2/4\pi r^4 \gg 1$). Figure 5 shows the stretching of a material line in a vortex with core (equations (78), (79)) after two and four turns, respectively.

(*d*) *Stretching and vorticity in extensional flow* (*axially symmetric swirling flow with uniform stretching*)

Turbulence can be conceived as a flow in which large integral steady values of vorticity $\boldsymbol{\omega}^2$ are obtained due to balance between intensification of vorticity by velocity gradients and loss by viscous dissipation. There are some exact solutions which illustrate these basic features and the contribution of local flows to material stretching and redistribution. Consider an axially symmetric swirling flow with uniform stretching (interpreted in a moving frame $\bar{F}$) described in cylindrical co-ordinates (r, θ, z) by

$$v_r = -\tfrac{1}{2}ar, \quad v_z = az, \quad v_\theta = v_\theta(r). \qquad (81), (82), (83)$$

This flow has a steady-state solution when

$$\frac{a}{2}r^2\omega + \nu r\frac{d\omega}{dr} = 0 \qquad (84)$$

(Batchelor 1967, p. 272), with a velocity distribution

$$\omega = \omega_0 \exp\left(-\frac{ar^2}{4\nu}\right), \qquad (85)$$

where ω_0 is a constant, and a swirl velocity given by

$$v_\theta = \frac{2\nu\omega_0}{ar}\left(1 - \exp\left(-\frac{ar^2}{4\nu}\right)\right). \qquad (86)$$

The viscous dissipation is produced by both acceleration contributions $\nabla.\mathbf{a}$ and vorticity contributions $\boldsymbol{\omega}^2$. This is a highly efficient flow (elongational character) with

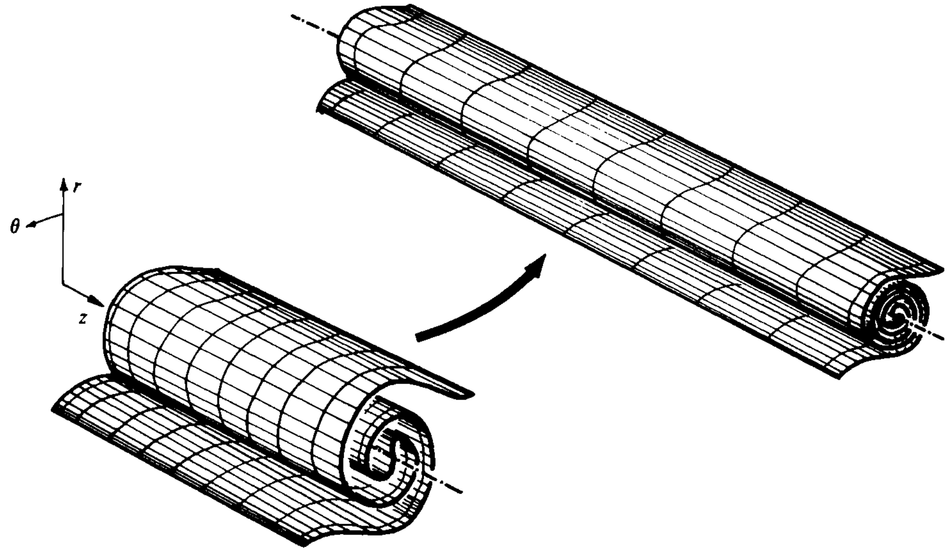

FIGURE 6. Stretching of a material plane in an axially symmetric swirling flow with uniform stretching. The figure shows the deformation of a plane with initial orientation $\{\hat{\mathbf{N}}\} \equiv \mathbf{e}_r$. Only the planes perpendicular to z are not exponentially stretched and concentric surfaces not distributed. The striation-thickness distribution increases as r^3 for $t \gg 0$ (see figure 5).

redistribution contributions (rotation). Figure 6 shows the effects of such a flow on a material surface.

The accelerational contribution is given by

$$\nabla . \mathbf{a} = \tfrac{3}{2}a^2 - \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{v_\theta^2}{r} r\right), \tag{87}$$

whereas the total viscous dissipation is given by

$$\mathbf{D} : \mathbf{D} = \tfrac{3}{2}a^2 - \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{v_\theta^2}{r} . r\right) + \frac{1}{2r^2}\left[\frac{\partial}{\partial r}(r v_\theta)\right]^2. \tag{88}$$

The simpler flow

$$v_r = -\tfrac{1}{2}ar, \quad v_z = az, \quad v_\theta = 0 \qquad (89), (90), (91)$$

has a viscous dissipation produced only by accelerational contributions $(\nabla . \mathbf{a}) = \mathbf{D} : \mathbf{D}$,

$$\epsilon = 3\mu a^2, \tag{92}$$

and has no rotational contribution.

The stretching of a material line is given by

$$L(t) \simeq L_0 \exp(at), \tag{93}$$

with an upper bound given by

$$L(t) = L_0 \exp\left(\left(\frac{\epsilon}{2\mu}\right)^{\frac{1}{2}} t\right) = L_0 \exp\left((\tfrac{3}{2})^{\frac{1}{2}} at\right). \tag{94}$$

The stretching of a material plane is given by

$$A(t) \simeq A_0 \exp(\tfrac{1}{2}at). \tag{95}$$

The upper bound is given by

$$A(t) = A_0 \exp\left(\left(\tfrac{3}{2}\right)^{\frac{1}{2}} at\right). \tag{96}$$

The swirling flow produces an elongation similar to the vortex decay that is uniformly compressed towards $t = 0$ by the action of v_r. The striation-thickness distributions generated by the two motions can be made equal in terms of a dimensionless parameter that takes into account the uniform stretching. That is,

$$s = s(r) \quad \text{in vortex decay;} \tag{97}$$

$$s = s(\xi), \quad \xi = \frac{r}{E(t)}, \quad E(t) = \exp\left(-\tfrac{1}{2}at\right), \tag{98}$$

in swirling flow with uniform stretching. It is not known what the general conditions are for this similarity behaviour.

An estimate of material-stretching in the swirling flow is given by the bounds of (93), (94) and (95), (96):

$$\exp(at) < L(t) < \exp\left(\left(\tfrac{3}{2}\right)^{\frac{1}{2}} at\right), \tag{99}$$

$$\exp\left(\tfrac{1}{2}at\right) < A(t) < \exp\left(\left(\tfrac{3}{2}\right)^{\frac{1}{2}} at\right). \tag{100}$$

Rotational contributions will improve the stretching given by (93), (94). The upper bound is given in terms of accelerational contribution.

Several other flows may be studied (see e.g. Uberoi 1979). Considerable benefit could arise from a detailed study of transport in such flows. Of special interest is the result of the integration over the space of a flow and over a distribution of flows. The existence of phenomena arising from distribution and interaction has been recognized. Flame-shortening is described by Marble & Broadwell (1977) as the phenomenon that occurs when two neighbouring reacting layers interact and quickly consume the intervening reactant. Isolation of reactants is described by Ottino (1980) as the phenomenon that occurs due to spatial stoichiometric distributions. In the context of this work and at the smallest scales these phenomena arise because of the distribution of material surfaces produced by the flow. Distributed and non-distributed striation-thickness distribution systems will react at different rates. Thus, reactants will be consumed rapidly in the layers surrounding the core of the vortex of figure 5. An irregular striation-thickness distribution will generate diffusional processes with length scales larger than s.

It should be emphasized that in the context of this approach the striation-thickness distribution is a dependent quantity of fluid-mechanical origin. It should be noted also that material surfaces are neither consumed nor annihilated but merely redistributed. The flame-shortening phenomena and isolation of reactants might be interpreted as a consequence of redistribution of material surfaces.

4. Conclusions

The objective has been the formulation and exploitation of a possible point of view for describing the mixing of diffusing and reacting fluids. Mixing descriptions based on the concepts of material surfaces and homeomorphic deformations are restricted solely to continuous motions and conveniently described by transport equations in

Lagrangian frames. The fluid-mechanical component of the mixing of multi-component diffusing and reacting fluids can be interpreted in terms of the deformation of material surfaces (tracers). It forms the basis of the fluid-dynamics–transport–chemical-reaction interaction. Consideration of the mechanical component (deformation) as the independent variable is particularly appealing if the hydrodynamics is scarcely affected by the transport and chemical-reaction processes.

Hardly anything of general value can be said concerning the local flow distribution without specific reference to the particular physical situation. The intermaterial-area redistribution seems to be related to vorticity and large-scale motions whereas the fluid dynamics–transport–reaction interaction is governed by small-scale flows whose stretching capacity is related to local viscous dissipation.

Application of the framework is not difficult as computations based on similar ideas (insofar as the level of complexity is concerned) have been shown to be possible. Applications of a lamellar model to homogeneous combustion are presented by Spalding (1978*b*), while a comparison with experimental measurements for the case of fast acid–base reaction mixing in a tubular reactor is presented by Ottino (1981).

Within the framework of the present description the following problems are of interest.

(*a*) *Effects of local motion on reaction schemes*

Chemical reactions are in general affected by mixing. Average values of conversion, yield, selectivity and product distribution depend on the interactions between small-scale local flows, mass and energy transfer, and chemical kinetics. Knowledge of these interactions can be obtained in principle by judicious selection of local flows and through corresponding solutions of the mass-transport and energy-transport equations (16), (17).

(*b*) *Fluid-mechanical mixing-path design*

This topic, related to (*a*), is concerned with the fluid-mechanical history needed to produce a desired selectivity of a given product for a given chemical reaction scheme. Problems (*a*) and (*b*) are relevant to combustion, air pollution and chemical synthesis.

(*c*) *Local thermal or chemical explosion during mixing of unpremixed fast reactions*

Mixing distribution and high generation of contact area (intensive stretching of material surfaces) might result in distributed interdiffusion and rate of reaction eventually surpassing dissipative effects. Local thermal or chemical explosions can be generated by this mechanism. This problem is especially relevant to combustion and reaction engineering.

Appendix. Transformation of the convective diffusion equation

Here we present the transformation of (61) written as

$$\frac{\partial c}{\partial t}+\alpha y\frac{\partial c}{\partial y}=D\frac{\partial^2 c}{\partial y^2}+\frac{D}{y}\frac{\partial c}{\partial y}+\hat{c}, \qquad \text{(A 1)}$$

where $\alpha = \mathbf{D}:\mathbf{e}_1\mathbf{e}_1$ and c stands for ρ_α. Use the transformations

$$\tau = \tau(y,t), \quad y = y(\tau,\xi); \tag{A 2}$$

$$\xi = \xi(y,t), \quad t = t(\tau,\xi); \tag{A 3}$$

and compute

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \tau}\frac{\partial \tau}{\partial t} + \frac{\partial c}{\partial \xi}\frac{\partial \xi}{\partial t}, \tag{A 4}$$

$$\frac{\partial c}{\partial y} = \frac{\partial c}{\partial \tau}\frac{\partial \tau}{\partial y} + \frac{\partial c}{\partial \xi}\frac{\partial \xi}{\partial y}, \tag{A 5}$$

$$\frac{\partial^2 c}{\partial y^2} = \frac{\partial c}{\partial \tau}\frac{\partial^2 \tau}{\partial y^2} + \frac{\partial^2 c}{\partial \tau^2}\left(\frac{\partial c^2}{\partial y}\right) + 2\left(\frac{\partial^2 c}{\partial \xi\,\partial \tau}\right)\frac{\partial \tau}{\partial y}\frac{\partial \xi}{\partial y} + \frac{\partial c}{\partial \xi}\frac{\partial^2 \xi}{\partial y^2} + \frac{\partial^2 c}{\partial \xi^2}\left(\frac{\partial \xi}{\partial y}\right)^2. \tag{A 6}$$

Consider

$$\frac{\partial \tau}{\partial y} = 0, \tag{A 7}$$

and impose

$$\frac{\partial \tau}{\partial t} = D\left(\frac{\partial \xi}{\partial y}\right)^2, \tag{A 8}$$

$$\frac{\partial \xi}{\partial t} + \alpha y\frac{\partial \xi}{\partial y} = D\frac{\partial^2 \xi}{\partial y^2}. \tag{A 9}$$

Equations (A 8) and (A 9) will be valid if no contradiction occurs. From (A 7) and (A 8) respectively

$$\tau = \tau(t), \quad \frac{\partial \xi}{\partial y} = h(t), \tag*{(A 10), (A 11)}$$

where $h(t)$ is a function of t. From (A 11)

$$\frac{\partial^2 \xi}{\partial y^2} = 0, \tag{A 12}$$

and by combination of (A 9) and (A 12)

$$\frac{\partial \xi}{\partial t} + \alpha y\frac{\partial \xi}{\partial y} = 0. \tag{A 13}$$

From (A 11)

$$\xi = h(t)\,y + \text{const.}, \tag{A 14}$$

where const. = 0 without loss of generality.

By substitution of (A 11) and (A 14) into (A 13)

$$\frac{dh(t)}{dt} + \alpha h(t) = 0, \tag{A 15}$$

$$\alpha = -\frac{d\ln h(t)}{dt} = \frac{d\ln s(t)}{dt}, \quad s(t) = (h(t))^{-1}. \tag{A 16}$$

From (A 8) and (A 11)

$$\frac{dt}{d\tau} = \frac{s^2(t)}{D}. \tag{A 17}$$

Then by (A 14)

$$\frac{D}{y}\frac{\partial c}{\partial \xi}\frac{\partial \xi}{\partial y} = \frac{d\tau}{dt}\frac{1}{\xi}\frac{\partial c}{\partial \xi}. \tag{A 18}$$

Substitution of (A 4)–(A 6) into (A 1) and use of the results (A 7)–(A 9) and (A 18) gives

$$\frac{\partial c}{\partial \tau}=\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial c}{\partial \xi}\right)+\left(\frac{dt}{d\tau}\right)\hat{c}, \tag{A 19}$$

which corresponds to (61). The proof of (60) is entirely similar.

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