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A Framework for Description of Mechanical Mixing of Fluids

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Mechanical mixing of fluids interpreted as deformation of contact interfaces between materials or originally designated material surfaces, can be described by continuum mechanical arguments. The idea is developed at two levels.

Part I: Exact kinematical description of mixing of fluids with negligible interfacial tension.
Part II: Description of mixing of fluids with negligible interfacial tension in terms of intermaterial area density.

The approach provides a unified mathematical description of the mechanical mixing of fluids.

SCOPE

Liquid-liquid mixing is a broad and important subject covering a variety of coupled physical phenomena: fluid mechanics, diffusion, and chemical reaction. Important special cases are obtained by the presence or absence of one or two of these three mechanisms. Mixing without diffusion is important in the processing of viscous liquids; mixing with diffusion and complex chemical reactions is an essential part of reaction engineering analysis; and mixing in turbulent flow fields is relevant to the fields of combustion, air pollution and atmospheric science.

However, mixing of fluids has lacked a sound theoretical description, due in large measure to coupling of processes and the complex geometry and time dependent topology of the mixing of moving fluids. Understanding and modeling of the physics of mixing has lagged far behind practical applications. Theories, models, and experiments suggested by a sufficient analytical description are now needed to supply at least qualitative understanding. Customarily different mixing processes are treated by different theories. With few exceptions no attempt has been made to propose a unified view. The consequences of a unified view would be a correct framing with a single perspective for a variety of physical phenomena which on first viewing appear to be unrelated.

This work presents a mathematical description of mechanical mixing of fluids. The only restriction to the analysis is the one of negligible interfacial tension between the fluids being mixed, i.e., "drop formation" is not allowed.

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CONCLUSIONS AND SIGNIFICANCE

Mixing operations are the heart of many industrial operations. Yet there has been relatively little study of mixing processes from the stand-point of classical fluid mechanics. This work details a framework of description based on the primitive concept of material surfaces, independent of the recognition of molecular diffusion (cf. Batchelor, 1967, p. 29 and p. 79) and only dependent on the existence of continuous fluid motions.

Mechanical mixing interpreted as deformation of material interfaces can be exactly described with the mathematical structure of continuum mechanics. This structure provides insight concerning cooperative action between velocity gradients, originates definitions of efficiency of mixing, highlights the role of initial material orientation, and suggests the need for reorienting intermaterial areas and periodic motions to improve mixing. Discussion of the material structures produced by continuous deformation leads to a lamellar structure assumption and to a structured continuum description of mixing of mutually soluble reacting and non-reacting fluids. Upper bounds for mechanical mixing generation are provided for two systems of chemical engineering interest: closed volume systems (e.g., stirred tanks), and open flow systems (e.g., pipe flows and tubular reactions).

Mixing without diffusion is particularly important in the processing of viscous liquids, but there are few developments of the theory dealing with this subject. Spencer and Wiley (1951) have attempted an analysis of deformation of interfaces. Mohr et al (1957) introduced a useful concept—the distance between components, or striation thickness. Their analysis is a simplified, local two-dimensional study which makes other more general applications rather complex and obscure. On the other hand, Middleman (1977) presents a more advanced study, but his analysis is restricted to some particular situations which are analyzed in detail.

With the possible exception of specialized treatments of turbulent motion, mixing has not received serious consideration within the context of general fluid mechanics. There is presently a serious imbalance between available experimental information and theoretical understanding (for example, Nagata, 1975; Uhl and Gray, 1966-1967). However, the basic kinematical tools for the analysis of the deformation and orientation of interfaces has been available for a long time (for example, references in Truesdell and Toupin, 1960). These tools are considered basic for the developments presented here.

Our purpose is to show how the rather vaguely defined notion of "mixing" of fluids can be analyzed within a rational setting. Thus, we shall attempt to bring into focus those elements of continuum mechanics that we believe form a basic framework for analysis of mixing problems. A second objective is to provide a basic vocabulary which may be used to describe the process of mixing. Particular emphasis will be placed on continua for which the motion is known. We shall assume that the materials which undergo mixing are immiscible so that their interfaces are clearly defined. We shall also assume that the interfacial surface tension is negligible; thus, the stress field is continuous throughout the medium (i.e., there is no jump at the interfaces) and we restrict our considerations to topological motions in which drop formation is not allowed. Further, we consider neither diffusion nor chemical reaction. However, these phenomena can readily be added to the framework developed here (Ottino, 1979). [It should be noted that immiscibility is not required if the concept of material surfaces is used. A material surface can be defined irrespective of the existence of molecular diffusion. The mechanical component of mixing is computed as deformations of initially designated material surfaces.]

Given an initial exact location of the interfaces separating the materials to be mixed, a major problem of mixing theory concerns a precise description of the location at any time of the homeomorphic transformation of these surfaces in space. We begin with a review of some kinematical concepts from continuum mechanics. Also discussed are three basic inequalities that have a bearing on much of the remainder of the discussion.

The analysis of mixing admits two levels of knowledge: (i) the whole motion that produces mixing is known; and (ii) only external macroscopic parameters are known, e.g., power input to produce mechanical stirring.

When the motion is known, the deformation of finite material lines and surfaces can be treated quantitatively. A way of quantification of the mixing efficiency of these deformations is illustrated with examples, showing efficiencies of shear and elongational flows. Continual reorientation of material surfaces with respect to the flow to produce better use of the motions is discussed followed by the possibility of recognizing mixing flows of high local efficiency index.

In most mixing operations the details of the motion are not known, however, it is still possible to carry out analysis with the assumption that the mixture has a lamellar structure. This assumption and two quantities which characterize such mixtures, intermaterial area density and striation thickness, are also discussed. Integral formulas are developed for these quantities. Average efficiency indices are described as well.

Preliminary Formulations

Kinematical Considerations from Continuum Mechanics (cf., Truesdell and Toupin, 1960).

By a motion of a body, we mean a smooth mapping

$$\underset{\sim}{x} = \underset{\sim}{\chi}(\underset{\sim}{X}, t), \quad \underset{\sim}{X} = \underset{\sim}{\chi}(\underset{\sim}{X}, 0) \tag{1}$$

where $\underset{\sim}{x}$ denotes the point in space occupied at time t by the particle which occupies $\underset{\sim}{X}$ at time $t = 0$. We require this motion to be a topological transformation so that the boundary of every body is a material surface throughout its motion. In particular then, the interface separating two different fluids is herein restricted to be a material surface. [It is worth noting, however, that an interface need not be a material surface if it is considered in the neighborhood of a solid boundary. In particular a contact line need not be a material line (Dussan and Davis, 1974).] When the motion fails to be topological, boundaries may be instantly created or destroyed, an example of which is the formation or coalescence of drops in a fluid. Thus mixing of fluids *with* the inclusion of surface tension might require the introduction of nontopological motions.

The nonsingular deformation gradient $\underset{\approx}{F}(\underset{\sim}{X}, t)$ and the velocity gradient $\underset{\approx}{L}(\underset{\sim}{X}, t)$ associated with the motion $\underset{\sim}{\chi}$ are defined respectively by:

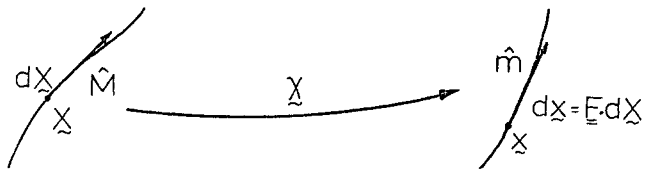

Figure 1a. Stretching of a differential material filament at $\underline{X}$ of length $|d\underline{X}|$ and orientation $\hat{M}$ to a point $\underline{x}$ at present time t with length $|d\underline{x}|$ and orientation $\hat{m}$ produced by the motion $\underline{\chi}$.

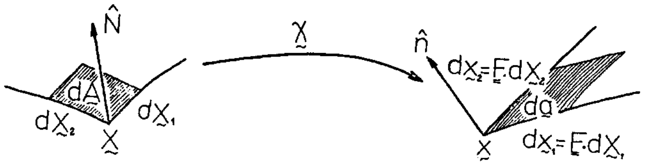

Figure 1b. Stretching of a differential material plane at $\underline{X}$ of area $d\underline{A}$ and orientation $\hat{N}$ to a point $\underline{x}$ at present time t with area $d\underline{a}$ and orientation $\hat{n}$ produced by the motion $\underline{\chi}$.

$$\underline{\underline{F}} = \nabla\underline{\chi}, \quad \underline{\underline{L}} = grad\ \dot{\underline{x}}, \tag{2}$$

where an over-dot $(\cdot)$ denotes material time differentiation. The operation ∇ denotes partial differentiation with respect to $\underline{X}$ whereas *grad* denotes partial differentiation with respect to $\underline{x}$. The lineal stretch $\lambda(\underline{X}, t)$ of an initial differential material filament at $\underline{X}$ (Figure 1a) of length $|d\underline{X}|$ and orientation $\hat{M}$ to a point $\underline{x}$ at the present time t with length $|d\underline{x}|$ and orientation $\hat{m}$ is given by:

$$\lambda \equiv \frac{|d\underline{x}|}{|d\underline{X}|} \tag{3}$$

Thus, λ is related to the motion by (for derivations see Appendix A):

$$\lambda = \sqrt{\underline{\underline{C}}:\hat{M}\hat{M}}, \quad \underline{\underline{C}} = \underline{\underline{F}}^T \cdot \underline{\underline{F}}, \tag{4}$$

and it readily follows that the present orientation $\hat{m}$ is related to the motion by:

$$\hat{m} = \underline{\underline{F}} \cdot \frac{\hat{M}}{\lambda} \tag{5}$$

The area stretch $\eta(\underline{X}, t)$ of an initial infinitesimal material surface (Figure 1b) at $\underline{X}$ of initial area $|d\underline{A}|$ and normal orientation $\hat{N}$ to its area $|d\underline{a}|$ and normal orientation $\hat{n}$ is given by

$$\eta \equiv \frac{|d\underline{a}|}{|d\underline{A}|} \tag{6}$$

Thus, η is related to the motion by:

$$\eta = \sqrt{(det\ \underline{\underline{F}})^2 \underline{\underline{C}}^{-1}:\hat{N}\hat{N}} \tag{7}$$

and the normal orientation $\hat{n}$ is related to the motion by:

$$\hat{n} = \frac{(det\ \underline{\underline{F}})\ (\underline{\underline{F}}^{-1})^T \cdot \hat{N}}{\eta} \tag{8}$$

It can be shown that

$$\dot{\hat{m}} = (\underline{\underline{D}} + \underline{\underline{\Omega}}) \cdot \hat{m} - (\underline{\underline{D}}:\hat{m}\hat{m})\hat{m} \tag{9}$$

where $\underline{\underline{D}}$ and $\underline{\underline{\Omega}}$ are the stretching and vorticity tensors, respectively, and are given by:

$$\underline{\underline{D}} = \tfrac{1}{2}(\underline{\underline{L}} + \underline{\underline{L}}^T), \quad \underline{\underline{\Omega}} = \tfrac{1}{2}(\underline{\underline{L}} - \underline{\underline{L}}^T) \tag{10}$$

A set of instantaneous directions of extreme stretching of differential material filaments $\hat{d}_1$, $\hat{d}_2$, and $\hat{d}_3$ are obtained as orthonormal solutions of the eigenvalue problem:

$$\underline{\underline{D}} \cdot \hat{d}_i = \lambda_i \hat{d}_i \quad i = 1, 2, 3 \tag{11}$$

and the corresponding instantaneous rate of rotation of this set is given by combination of Eqs. 9 and 11 as:

$$\dot{\hat{d}}_i = \underline{\underline{\Omega}} \cdot \hat{d}_i \quad i = 1, 2, 3 \tag{12}$$

The material time rates of lineal and area stretch per unit of present lineal and area stretch are given respectively by:

$$\frac{\dot{\lambda}}{\lambda} = \underline{\underline{D}}:\hat{m}\hat{m} \tag{13}$$

and

$$\frac{\dot{\eta}}{\eta} = div\ \underline{v} - \underline{\underline{D}}:\hat{n}\hat{n} \tag{14}$$

The area and lineal stretches are related for $\hat{m} = \hat{n}$ by:

$$\lambda\eta = det\ \underline{\underline{F}} \tag{15}$$

For isochoric motions (e.g., those motions allowable for incompressible materials), $det\ \underline{\underline{F}} = 1$ and

$$\lambda\eta = 1 \tag{16}$$

In what follows the discussion will be restricted to this class of motions. The maximum material time rates of lineal and area stretch per unit of present lineal and area stretch are given instantaneously by:

$$\left.\frac{\dot{\lambda}}{\lambda}\right|_{\max} = (\underline{\underline{D}}:\hat{m}\hat{m})_{\max}$$
$$\left.\frac{\dot{\eta}}{\eta}\right|_{\max} = (-\underline{\underline{D}}:\hat{n}\hat{n})_{\max} \tag{17}$$

The local instantaneous orientations $\hat{m}$ and $\hat{n}$ are given for any stretching tensor $\underline{\underline{D}}$ as one of the solutions of Eq. 11.

Inequalities. It is convenient to record for later use the following inequalities (e.g., Hardy et al., 1973).

1) The Cauchy-Schwarz inequality implies that:

$$\underline{\underline{T}}:\hat{e}\hat{e} \leq |(\underline{\underline{T}}:\underline{\underline{T}})^{\frac{1}{2}}| \tag{18}$$

where $\underline{\underline{T}}$ is any tensor and $\hat{e}$ is any unit vector.

2) The Hölder inequality implies that:

$$(\textstyle\int_{\mathfrak{S}} f(\underline{x})dv)^k \geq \int_{\mathfrak{S}} (f(\underline{x}))^k dv \tag{19}$$

where $f(\underline{x})$ is a scalar function defined on the finite volume $\mathfrak{S}$ and where k is such that $0 < k < 1$.

3) The Jensen inequality implies that:

$$\textstyle\int_{\mathfrak{S}} ln\ f(\underline{x})dv \leq ln[\int_{\mathfrak{S}} f(\underline{x})dv] \tag{20}$$

where $f(\underline{x})$ is a scalar function defined on the finite space $\mathfrak{S}$.

PART I: KINEMATICS OF MIXING OF FLUIDS BY KNOWN MOTIONS

Deformation of Finite Material Lines and Surfaces

The mathematical description of the homeomorphic transformations of finite material surfaces and lines is an exact description of mechanical mixing. This section introduces some basic vocabulary and analyzes the necessary mathematical structure for such description.

The configuration of a smooth material surface $\mathfrak{S}$ characterized by $f(\underline{x}, t) = 0$ at any time t is initially at $t = 0$ defined by the set of unit vector orientation $\{\hat{N} = \hat{N}(\underline{X}):\hat{N}$ normal to surface $\mathfrak{S}\}$ denoted $\{\hat{N}\}$ where $\underline{X}$ identifies the location in space of the material particles. Equivalently $\mathfrak{S}$ can be defined by its initial location $f(\underline{X}, 0) = 0$.

The configuration of a smooth material line $\mathscr{L}$ is defined by $g(\underline{x}, t) = 0 \cap h(\underline{x}, t) = 0$. $\mathscr{L}$ is uniquely characterized by the set $\{\hat{M} = \hat{M}(\underline{X}):\hat{M}$ tangent unit vector at each point $\{\underline{X}\}\}$ where $\underline{X}$ denotes the initial location of the material particles. Equivalently $\mathscr{L}$ can be defined by its initial location $g(\underline{X}, 0) = 0 \cap$

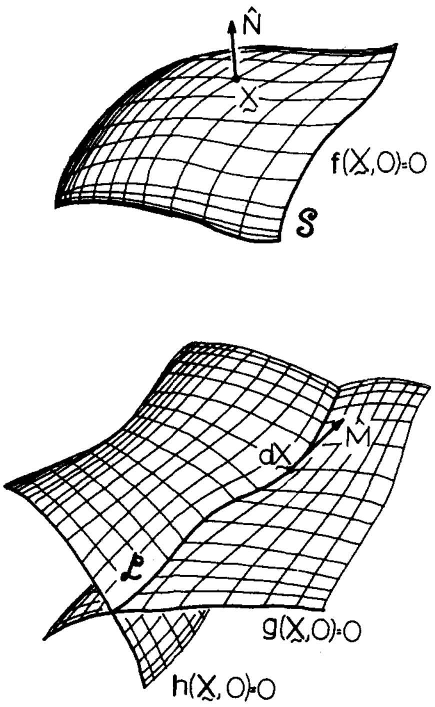

Figure 2. Representation of material surface with local orientation $\hat{N} = \hat{N}(\underset{\sim}{X})$ and material line with local orientation $\hat{M} = \hat{M}(\underset{\sim}{X})$.

$h(\underset{\sim}{X}, 0) = 0$. Both concepts are pictured in Figure 2. Set $\mathfrak{S}_0$ denotes $\{\underset{\sim}{X}: f(\underset{\sim}{X}, 0) = 0\}$ whereas set $\mathscr{L}_0$ denotes $\{\underset{\sim}{X}: g(X, 0) = 0 \cap h(\underset{\sim}{X}, 0) = 0\}$. Notations $\mathfrak{S}_t$ and $\mathscr{L}_t$ refer to the configuration of material surfaces and lines at time t, respectively.

The area at time t of the material surface $\mathfrak{S}$ with initial orientation $\{\hat{N}\}$ is denoted $A(\{\hat{N}\}, t)$. The length at time t of the material line $\mathscr{L}$ with initial orientation $\{\hat{M}\}$ is denoted $L(\{\hat{M}\}, t)$.

The mean values over $\mathfrak{S}_0$ and $\mathscr{L}_0$ of a function $p(\underset{\sim}{X}, t)$ defined over $\mathfrak{S}_0$ and $\mathscr{L}_0$ for any time t are given by:

$$\langle p \rangle_{\mathfrak{S}_t} = \frac{\int_{\mathfrak{S}_0} p(\underset{\sim}{X}, t)|d\underset{\sim}{A}|}{\int_{\mathfrak{S}_0}|d\underset{\sim}{A}|}, \quad \langle p \rangle_{\mathscr{L}_t} = \frac{\int_{\mathscr{L}_0} p(\underset{\sim}{X}, t)|d\underset{\sim}{X}|}{\int_{\mathscr{L}_0}|d\underset{\sim}{X}|} \tag{21}$$

for $p(\underset{\sim}{X}, t) = \eta(\underset{\sim}{X}, t)$ on $\mathfrak{S}_0$ we find:

$$\langle \eta \rangle_{\mathfrak{S}_0} = 1 \tag{22}$$

for $p(\underset{\sim}{X}, t) = \eta(\underset{\sim}{X}, t)$ on $\mathscr{L}_0$ we find:

$$\langle \lambda \rangle_{\mathscr{L}_0} = 1 \tag{23}$$

Using mean values (Eq. 21) we have:

$$\langle \eta \rangle_{\mathfrak{S}_t} = \frac{A(\{\hat{N}\}\ t)}{A(\{\hat{N}\}, 0)}, \quad \langle \lambda \rangle_{\mathscr{L}_t} = \frac{L(\{\hat{M}\}, t)}{L(\{\hat{M}\}, 0)} \tag{24}$$

The length of a material line $\mathscr{L}$ joining the points $\underset{\sim}{X}_1$, $\underset{\sim}{X}_2$, is computed as a function of time by:

$$L(\{\hat{M}\}, t) = \int_{\mathscr{L}_0} \sqrt{\underset{\approx}{C}:\hat{M}\hat{M}}|d\underset{\sim}{X}| \tag{25}$$

The area of a finite regular material surface is computed as a function of time by:

$$A(\{\hat{N}\}, t) = \int_{\mathfrak{S}_0} \sqrt{(det\ \underset{\approx}{F})^2 \underset{\approx}{C}^{-1}:\hat{N}\hat{N}}|d\underset{\sim}{A}| \tag{26}$$

Deformation of finite material surfaces in a motion $\underset{\sim}{\chi}$ is pictured in Figure 3.

Bounds for area, length, and rates of stretching can be obtained by use of inequalities (Eqs. 18-20), definitions (Eq. 21), and kinematical formulas. We exemplify the method by a length inequality. Eq. 13 is written as:

$$\dot{\overline{ln\ \lambda(\underset{\sim}{X}, t)}} = \underset{\approx}{D}:\hat{m}\hat{m} \tag{27}$$

where $\underset{\approx}{D}:\hat{m}\hat{m}$ is computed as a function of $\underset{\sim}{X}$, t by use of Eqs. 2, 5 and 10.

We have by Inequality (Eq. 18):

$$\underset{\approx}{D}:\hat{m}\hat{m} \leq (\underset{\approx}{D}:\underset{\approx}{D})^{\frac{1}{2}} \tag{28}$$

where the square root is taken with the positive sign. By definition (Eq. 21) and Inequality (Eq. 19) we obtain:

$$\langle \underset{\approx}{D}:\hat{n}\hat{n} \rangle_{\mathscr{L}_t} \leq \langle (\underset{\approx}{D}:\underset{\approx}{D})^{\frac{1}{2}} \rangle_{\mathscr{L}_t} \leq \langle \underset{\approx}{D}:\underset{\approx}{D} \rangle^{\frac{1}{2}}_{\mathscr{L}_t} \tag{29}$$

and consequently

$$\int_0^t \langle \underset{\approx}{D}:\hat{n}\hat{n} \rangle_{\mathscr{L}_t} dt' \leq \int_0^t \langle \underset{\approx}{D}:\underset{\approx}{D} \rangle^{\frac{1}{2}}_{\mathscr{L}_t} dt' \tag{30}$$

Thus:

$$\langle ln\ \lambda(\underset{\sim}{X}, t) \rangle_{\mathscr{L}_t} \leq \int_0^t \langle \underset{\approx}{D}:\underset{\approx}{D} \rangle^{\frac{1}{2}}_{\mathscr{L}_t} dt'. \tag{31}$$

Inequality (Eq. 20) and Eq. 24 imply:

$$\langle ln\ \lambda(\underset{\sim}{X}, t) \rangle_{\mathscr{L}_t} \leq ln \langle \lambda(\underset{\sim}{X}, t) \rangle_{\mathscr{L}_t} = ln\ \frac{L(\{\hat{M}\}, t)}{L(\{\hat{M}\}, 0)} \tag{32}$$

Therefore, in general it is *not* possible to conclude that:

$$L(\{\hat{M}\}, t) < L(\{\hat{M}\}, 0)\ \exp \int_0^t \langle \underset{\approx}{D}:\underset{\approx}{D} \rangle^{\frac{1}{2}}_{\mathscr{L}_t} dt' \tag{33}$$

The motivation for the derivation of this formula is provided by the exponential stretching of material lines in turbulent flows (Batchelor, 1952) where for long times he wrote:

$$L(\{\hat{M}\}, t) \sim L(\{\hat{M}\}, 0)\ \exp\ (\underset{\approx}{D}:\underset{\approx}{D})_{av} t$$

It is not clear from his work what type of average $(\underset{\approx}{D}:\underset{\approx}{D})_{av}$ is but presumably $\underset{\approx}{D}:\underset{\approx}{D}$ is considered to be uniform in space. In general to write such a formula it would be necessary to have a time independent value of $\underset{\approx}{D}:\underset{\approx}{D}$ over the material line $\mathscr{L}$.

We conclude this section with formulas for time derivatives of length and area of finite material lines and surfaces. The material time derivative of the length of a finite material line is given by (Fosdick, 1979).

$$\dot{\overline{L(\{\hat{M}\}, t)}} = \underset{\sim}{v} \cdot \hat{m} \Big|_{\underset{\sim}{x}_0}^{\underset{\sim}{x}_1} - \int_{\mathscr{L}_t} K_{\mathscr{L}} \underset{\sim}{v} \cdot \hat{a} |d\underset{\sim}{x}| \tag{34}$$

where $\hat{m}$ is a tangent vector given by:

$$\hat{m} = \frac{d\underset{\sim}{x}}{|d\underset{\sim}{x}|}$$

and $K_{\mathscr{L}}$ is the curvature related to the normal by:

$$\frac{d\hat{m}}{|d\underset{\sim}{x}|} = K_{\mathscr{L}} \hat{a}$$

The vectors $\hat{m}$ (tangent), $\hat{a}$ (normal), together with $\hat{b}$ (binormal) constitute the Frenet triad defined for each point of the line (Figure 4a).

The material time derivative of the area of a finite material surface is given by (Fosdick, 1979):

$$\dot{\overline{A(\{\hat{N}\}, t)}} = \int_{\partial\mathfrak{S}_t} (\hat{\sigma} \times \hat{n}) \cdot \underset{\sim}{v} |d\underset{\sim}{a}| - \int_{\mathfrak{S}_t} (\underset{\sim}{v} \cdot \hat{n}) K_{\mathfrak{S}} |d\underset{\sim}{a}| \tag{35}$$

where $\hat{n}$ is a normal vector to the surface and the curvature $K_{\mathfrak{S}}$ is defined as:

$$K_{\mathfrak{S}} = -\ div_{\mathfrak{S}_t} \hat{n}$$

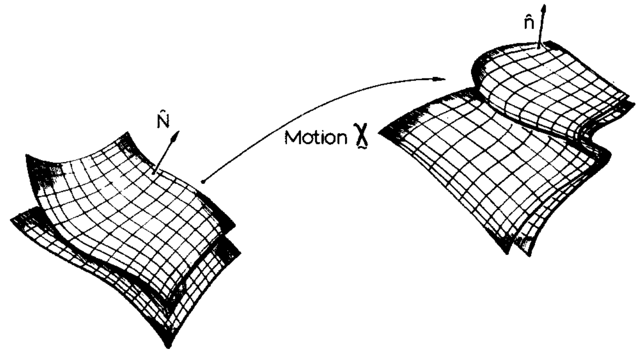

Figure 3. Deformation of material surfaces in a topological motion $\underset{\sim}{\chi}$.

The vector $\hat{\sigma}$ is a tangent vector to the boundary of the surface, such that it is right-hand oriented with respect to $\hat{n}$. (Figure 4b)

Two special cases of the above formulas are of interest: (i) The ends to the material surface are attached to nonmoving boundaries with static contact points. (ii) Loops of material lines (i.e., $\underset{\sim}{x}_1 = \underset{\sim}{x}_0$) and closed surfaces (i.e., $\partial\mathfrak{S}_t = \phi$). In these cases (*i, ii*), Eqs. 34 and 35 reduce to:

$$\overline{(L(\{\hat{M}\}, t)}^{\cdot} = - \int_{\mathscr{L}_t} K_{\mathscr{L}} \underset{\sim}{v} \cdot \hat{a} |d\underset{\sim}{x}| \tag{36}$$

$$\overline{(A(\{\hat{M}\}, t)}^{\cdot} = - \int_{\mathfrak{S}_t} (\underset{\sim}{v} \cdot \hat{n}) K_{\mathfrak{S}} |d\underset{\sim}{a}| \tag{37}$$

Local Efficiency Index for Mixing

Stretching of interfaces (mixing in our definition) is a cooperative action between velocity gradients and orientation. A mathematical formulation using this idea is developed next. Restricting our discussion to isochoric motions ($det\, \underline{\underline{F}} = 1$) and using Eqs. 4 and 7, we obtain for rate of area and length stretch:

$$\frac{\dot{\eta}}{\eta} = \tfrac{1}{2} \frac{\dot{\overline{\underline{\underline{C}}^{-1}}}:\hat{N}\hat{N}}{\underline{\underline{C}}^{-1}:\hat{N}\hat{N}} \qquad \frac{\dot{\lambda}}{\lambda} = \tfrac{1}{2} \frac{\dot{\underline{\underline{C}}}:\hat{M}\hat{M}}{\underline{\underline{C}}:\hat{M}\hat{M}} \tag{38}$$

whereas maximum rates are given by Eqs. 13, 14 and 18 as:

$$\left|\frac{\dot{\eta}}{\eta}\right| \leq (\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}} \qquad \left|\frac{\dot{\lambda}}{\lambda}\right| \leq (\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}} \tag{39}$$

Efficiency indices for mixing (or demixing) based on stretching of material surfaces or lines can now be defined by:

$$e_{\mathfrak{S}}(\hat{N}) = \frac{\tfrac{1}{2}\left|\dfrac{\dot{\overline{\underline{\underline{C}}^{-1}}}:\hat{N}\hat{N}}{\underline{\underline{C}}^{-1}:\hat{N}\hat{N}}\right|}{(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}} \qquad e_{\mathscr{L}}(\hat{M}) = \frac{\tfrac{1}{2}\left|\dfrac{\dot{\underline{\underline{C}}}:\hat{M}\hat{M}}{\underline{\underline{C}}:\hat{M}\hat{M}}\right|}{(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}} \tag{40}$$

By definition both $e_{\mathfrak{S}}$ and $e_{\mathscr{L}}$ are positive. For $\hat{N} = \hat{M}$, $\dot{\lambda}/\lambda + \dot{\eta}/\eta = 0$, and

$$|e_{\mathfrak{S}}| = |e_{\mathscr{L}}| = e \tag{41}$$

As an example, consider efficiency index e, in the case of shear and elongational flows.

Efficiency Index for Shear Flows. Consider a shear flow such that:

$$\begin{aligned} v_1 &= \dot{x}_1 = \frac{U}{H} x_2 & & & x_1 &= X_1 \\ v_2 &= \dot{x}_2 = 0 & &\text{when for } t = 0 & x_2 &= X_2 \\ v_3 &= \dot{x}_3 = 0 & & & x_3 &= X_3 \end{aligned} \tag{42}$$

where X_1, X_2, X_3 denote the location of a small material plane with orientation N_1, N_2, N_3.

It can be shown that:

$$[C_{ij}] = \begin{bmatrix} 1 & \dfrac{U}{H} t & 0 \\ \dfrac{U}{H} t & 1 + \left(\dfrac{U}{H} t\right)^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{43}$$

$$e = \frac{\tfrac{1}{2}\left| \dfrac{\dfrac{U}{H}\left[N_2N_1 + N_2\left[N_1 + 2\left(\dfrac{U}{H}\right)N_2 t\right]\right]}{N_1^2 + 2\left(\dfrac{U}{H}\right)N_1N_2 t + N_2^2\left[1 + \left(\dfrac{U}{H}t\right)^2\right] + N_3^2} \right|}{\sqrt{\dfrac{\left(\dfrac{U}{H}\right)^2}{2}}} \tag{44}$$

[For other (e.g. nonsteady) shear flows the reader is referred to Truesdell and Toupin (1960), p. 294 *et seq.*] Unless $N_1 = N_2 = 0$ in which case $e = 0$ and remains zero, the mixing efficiency index decays as t^{-1}. [For example, initially concentric cylindrical surfaces in a Couette apparatus.] A maximum value, corresponding to the eigenvalue problem $\underline{\underline{D}} \cdot \hat{n} = \lambda \hat{n}$, is reached when the angle between $\hat{n}$ and x_2 is 45°. For the initial orientation $N_1 = 0$, $N_2 = 1$, $N_3 = 0$; this value is 0.707.

Efficiency Index for Elongational Flows. Consider a steady, uniaxial, elongational flow such that:

$$\begin{aligned} v_1 &= \dot{x}_1 = \dot{\epsilon} x_1 & & & x_1 &= X_1 \\ v_2 &= \dot{x}_2 = -\frac{\dot{\epsilon}}{2} x_2 & &\text{where for } t = 0 & x_2 &= X_2 \\ v_3 &= \dot{x}_3 = -\frac{\dot{\epsilon}}{2} x_3 & & & x_3 &= X_3 \end{aligned} \tag{45}$$

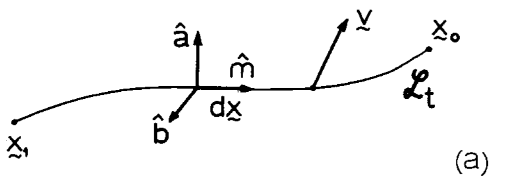

Figure 4a. Material line showing Frenet triad: $\hat{m}$ (tangent), $\hat{a}$ (normal) $\hat{b}$ (binormal). Observe that if curvature $K_{\mathscr{L}}$ is zero the instantaneous rate of length stretch is given by stretching at ends, i.e., Eq. 34 reduces to

$$\overline{L(\{M\}, t)}^{\cdot} = \underset{\sim}{v} \cdot \hat{m} \Big|_{\underset{\sim}{x}0}^{\underset{\sim}{x}1}.$$

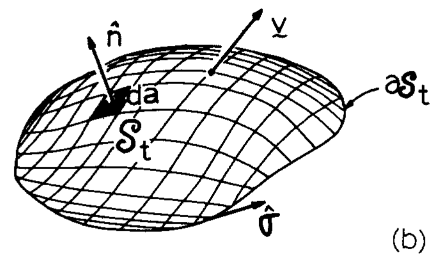

Figure 4b. Material surface showing vectors to compute area stretch. Observe that if curvature $K_{\mathfrak{S}}$ is zero the instantaneous rate of area growth is given by stretching computed at the boundaries, i.e., Eq. 35 reduces to

$$\overline{A(\{N\}, t)}^{\cdot} = \int_{\partial S_t} (\hat{\sigma} x \hat{n}) \cdot \underset{\sim}{v}\, d\underset{\sim}{a}.$$

X_1, X_2, X_3 denote the location of a small material plane with orientation N_1, N_2, N_3.

It can be shown that:

$$[C_{ij}] = \dot{\epsilon} \begin{bmatrix} 2e^{2\dot{\epsilon}t} & 0 & 0 \\ 0 & -e^{-\dot{\epsilon}t} & 0 \\ 0 & 0 & -e^{-\dot{\epsilon}t} \end{bmatrix} \tag{46}$$

and

$$e = \frac{1}{2\sqrt{6}} \frac{[2M_1^2 e^{3\dot{\epsilon}t} - M_2^2 - M_3^2]}{[M_1^2 e^{3\dot{\epsilon}t} + M_2^2 + M_3^2]} \tag{47}$$

Unless $N_1 = 0$, the efficiency index e tends to $\sqrt{1/6}$ or 0.408. Thus as measured by the index e, elongational flows are much more efficient than shear flows. This conclusion is of course independent of the nature of the fluid. Decay behavior t^{-1} in general shear flows (Poiseuille, Couette) can be partly solved by either reorienting the area or the motion. Further discussion of this point is given in the next section using the concept of separable motions.

More on Efficiency of Mixing: Global Efficiency Index. Present area of material surfaces and length of material lines deformed in a motion χ depends on initial orientations $\{\hat{N}\}$ and $\{\hat{M}\}$ (cf. 3.6 and 3.7). The same amount of area can be stretched differently depending on initial location. A way to study this dependency is to compare the amount of stretch of the same amount of surface or same length of line with different initial orientations, e.g., in optimum or nonoptimum initial orientation.

Another efficiency, $E_{\mathscr{L}}$, $E_{\mathfrak{S}}$, based on amount of stretch rather than on rate of stretch can be defined in the following way. Given a motion χ we define efficiencies which are functions of orientation and time as:

$$E_{\mathfrak{S}}(t) = \frac{A(\{\hat{N}\}, t)}{A(\{\hat{N}\}^*, t)} \quad E_{\mathscr{L}}(t) = \frac{L(\{\hat{M}\}, t)}{L(\{\hat{M}\}^*, t)} \tag{48}$$

Their meaning is the following: Given a surface $\mathfrak{S}_0$, or line $\mathscr{L}_0$, there exists an optimum orientation set $\{\hat{N}\}^*$ or $\{\hat{M}^*\}$ for the given motion χ which is compared with the actual initial orientation $\{\hat{N}\}$ or $\{\hat{M}\}$. The optimum orientation set $\{\hat{N}\}^*$ or $\{\hat{M}\}^*$ can be obtained as one of the solutions of the eigenvalue problems:

$$\underline{\underline{C}} \cdot \hat{M} = \lambda \hat{M} \text{ for all } \underline{X} \epsilon \mathscr{L}_0$$
$$\underline{\underline{C}}^{-1} \cdot \hat{N} = \lambda^{-1} \hat{N} \text{ for all } \underline{X} \epsilon \mathfrak{S}_0 \tag{49}$$

By definition $E_{\mathfrak{S}}(0) = E_{\mathscr{L}}(0) = 1$.

Example. Consider the shear flow given by Eq. 42. The length of a line with initial length L for orientation $\{\hat{M}\} = \{1, 0, 0\}$ $\underline{X} \epsilon \mathscr{L}$ is found to be:

$$L(\{\hat{M}\}, t) = \sqrt{L^2\left(1 + \left(\frac{V}{H}\right)^2 t^2\right)}$$

The length of a line with the same initial length but with optimum orientation $[\hat{M}]^* = [\sqrt{2}/2, \sqrt{2}/2, 0]$ $\underline{X} \epsilon \mathscr{L}$ at time t is found to be:

$$L(\{\hat{M}^*\}, t) = \sqrt{L^2\left(\frac{V}{H} t + 1 + \left(\frac{V}{H}\right)^2 \frac{t^2}{2}\right)}$$

Efficiency $E_{\mathscr{L}}$ is therefore:

$$E_{\mathscr{L}}(t) = \left[\frac{1 + \left(\frac{V}{H} t\right)^2}{1 + \frac{V}{H} t + \left(\frac{V}{H}\right)^2 \frac{t^2}{2}} \right]^{1/2}$$

which has the properties $E_{\mathscr{L}}(0) = 1$, $E_{\mathscr{L}}(\infty) = \sqrt{2}$.

Reorientation of Intermaterial Area

The most efficient way to mix, as measured by the local efficiency index, is in elongational flows with a proper initial orientation $\{\hat{N}\}$ or $\{\hat{M}\}$. Such flows can be obtained in the expanding sheets from collision of free jets of fluids to be mixed. In practice, however, there are restrictions. One is space between boundaries and time of flow. Another is the physical impossibility of elongational flows (which are irrotational) in flow systems with solid boundaries, the reason being that viscous fluids adhere to boundary surfaces. Motions confined by boundaries are rotational (Serrin, 1960, p. 148). These restrictions suggest the use of mixing cycles in which material is kept within reasonable physical space but where there is a periodic reorientation of intermaterial area. A continuous flow, which somehow gives a periodic reorientation of the intermaterial areas, must be confined by boundaries. However, flows with boundaries eventually become, after time

$$t = \frac{\text{characteristic flow channel dimension}}{\text{characteristic flow velocity}},$$

some type of shear flow showing inverse time decay in the intermaterial area generation rate. For example, for most initial orientations $\{\hat{N}\}$, the combinations of Couette and Poiseuille flows show this behavior.

The term $\underline{\underline{D}}:\hat{n}\hat{n}$ has maximum value when $\hat{n}$ coincides with the maximum principal rate of strain direction of the flow. Calculation of this orientation, in practice, should present no problem once the nature of the flow has been decided. One can generate efficient mixing if $\hat{n}$ (normal to material surfaces) varies direction near the maximum stretching direction, say $\hat{d}_1$. However, in general, $\hat{n}$ and $\hat{d}_1$ change direction at different speed (Eqs. 9 and 12). Nevertheless, use of this maximum stretch direction can be made in the following way: Consider a flow α that produces mixing during the time interval t_α $(0 \le t < t_\alpha)$ at some average value of $\underline{\underline{D}}:\hat{n}\hat{n}$ over the surfaces as close as possible to $(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}$. A second flow β can now be specified to produce efficient (in the sense of Eqs. 40) use of the final intermaterial area orientation $\hat{n}$ produced by the α flow, i.e., the principal stretching direction (field of vectors $\hat{d}_1 = \hat{d}_1(\underline{X})$) has to produce a maximum value of $\underline{\underline{D}}:\hat{n}\hat{n}$. In common parlance the first flow is "folded" into the second flow (Ranz, 1979). A properly designed flow system could eventually produce, on time scales much larger than t_i $(i = \alpha, \beta \ldots)$, a high stretch growth with a relatively high efficiency index.

The idea of mixing flow field composed of repetitive cyclic units can be put in more precise mathematical terms. Let us consider a motion χ that transforms the configuration of a body B from B_0 to B_t, i.e.,

$$\chi_t : B_0 \rightarrow B_t \tag{50}$$

and a set of motions

$$\chi_t^{(1)} : B_0 \rightarrow B_1$$
$$\chi_t^{(2)} : B_1 \rightarrow B_2$$
$$\chi_t^{(n)} : B_{n-1} \rightarrow B_n$$

such that their composition produces the motion χ_t.

$$\chi_t^{(n)} \cdot \chi_t^{(n-1)} \cdot \ldots \cdot \chi_t^{(1)}(\cdot) = \chi_t(\cdot) \tag{51}$$

The deformation gradients are related by:

$$\underline{\underline{F}} = \nabla \chi_t = \underline{\underline{F}}^{(n)} \cdot \underline{\underline{F}}^{(n-1)} \ldots \underline{\underline{F}}^{(1)}$$

and deformation, here exemplified for the case of lineal stretch, is consequently given by:

$$\lambda = \sqrt{\underline{F}^{(1)T} \cdot \underline{F}^{(2)T} \ldots \underline{F}^{(n)T} \ldots \underline{F}^{(n)} \ldots \underline{F}^{(2)} \cdot \underline{F}^{(1)} : \hat{N}\hat{N}} \tag{52}$$

Despite its complex appearance, this equation can be more useful than Eq. 4, which considers a single motion rather than its individual constituents since the tensors $\underline{F}^{(i)}$ can be considerably simpler than the deformation gradient of the whole motion, $\underline{F}$.

Complex flow fluids will mix and demix (stretch or shorten) depending on local values of $\underline{D}:\hat{n}\hat{n}$. On the average, a mixing motion has to produce a net increase of intermaterial area. Purely mechanical mixing is reversible. If motion $\underset{\sim}{x} = \chi(\underset{\sim}{X}, t)$ produces mixing the reverse motion $\underset{\sim}{x} = \chi(\underset{\sim}{X}, -t)$ will demix. However, if molecular diffusion is allowed, a mixing-demixing process is not possible. The reason for this is that diffusional processes are generally described by a parabolic differential equation that does not conserve form after substitution of time by minus time (Prigogine, 1955).

Criteria for Mixing Flows of High Local Efficiency Index

The maximum local rate of stretch $\dot{\eta}/\eta$ at a point $\underset{\sim}{X}$ belonging to a surface $\mathfrak{S}_t$ is achieved when $\hat{n} = \hat{n}(\underset{\sim}{X}, t)$, normal to the surface, coincides with one of the eigenvectors of $\underline{D} = \underline{D}(\underset{\sim}{X}, t)$, say $\hat{d}_i$. It is then desirable to keep $\hat{n} \cdot \hat{d}_i$ = function $(\underset{\sim}{X}, t)$ as close as possible to one (or minus one, depending on the choice of direction of $\hat{n}$). Periodic oscillations between one and minus one should be avoided since they imply mixing and demixing. Periodic oscillations between zero and one will eventually produce good mixing. We now analyze the possibility of a flow that produces $\hat{m} \cdot \hat{d}_1$ = const. for all $\underset{\sim}{X} \epsilon \mathfrak{S}$ for some initial orientation $\{\hat{N}\}$. Derivation will be shown for lineal stretch.

Scalar product constancy implies:

$$\dot{\hat{m}} \cdot \hat{d}_1 + \hat{m} \cdot \dot{\hat{d}}_1 = 0 \tag{53}$$

and using Eq. 9 and 12:

$$[(\underline{D} + \underline{\Omega}) \cdot \hat{m} - (\underline{D}:\hat{m}\hat{m})\hat{m}] \cdot \hat{d}_1 + \hat{m} \cdot \underline{\Omega} \cdot \hat{d}_1 = 0$$

Using the result of Eq. 38, $\underline{\Omega} = -\underline{\Omega}^T$, and Eq. 5, we get:

$$\left[(\underline{D} + \underline{\Omega}) \cdot \underline{F} \qquad \frac{(\dot{\underline{C}}:\hat{M}\hat{M})\underline{F}.\hat{M}}{\underline{C}:\hat{M}\hat{M}\ \lambda}\right] \cdot \hat{d}_1 - \underline{\Omega} \cdot \underline{F} \cdot \frac{\hat{M}}{\lambda} \cdot \hat{d}_1 = 0 \tag{54}$$

and

$$\left(\underline{D} \cdot \underline{F} - ½ \frac{\dot{\underline{C}}:\hat{M}\hat{M}}{\underline{C}:\hat{M}\hat{M}} \underline{F}\right) \cdot \hat{M} \cdot \hat{d}_1 = 0 \tag{55}$$

On the other hand, criterion $\hat{n} \cdot \hat{d}_1$ = const. produces:

$$\frac{(\underline{F} \cdot \hat{M}) \cdot \hat{d}_1}{(\underline{C}:\hat{M}\hat{M})^{\frac{1}{2}}} = \text{const.} \tag{56}$$

For $\hat{m} \cdot \hat{d}_1 = f(\underset{\sim}{X}, t)$, where f is a scalar function we have:

$$\left(\underline{D} \cdot \underline{F} - ½ \frac{\dot{\underline{C}}:\hat{M}\hat{M}}{\underline{C}:\hat{M}\hat{M}} \underline{F}\right) \cdot \hat{M} \cdot \hat{d}_1 = 0,$$

$$\frac{(\underline{F} \cdot \hat{M}) \cdot \hat{d}_1}{(\underline{C}:\hat{M}\hat{M})^{\frac{1}{2}}} = f \tag{57}$$

Given a motion χ, $\underline{F}$, $\underline{C}$, $\dot{\underline{C}}$, $\underline{D}$ and $\hat{d}_1$ can be calculated. Different sets of initial orientation $\{M\}$ can be checked using the above equations. Motions characterized by a non-decaying value of f for some orientation $\{\hat{M}\}$ are good mixing flows.

Conclusions of Part I

Mechanical mixing interpreted as deformation of material planes and lines can be exactly described with the mathematical structure of continuum mechanics. This structure provides insight concerning cooperative action between velocity gradients and orientation of surfaces and lines, originates definitions of local efficiency index for mixing, highlights the role of initial orientation, and suggests the need for reorienting intermaterial areas and periodic motions to improve mixing. Simple arguments lead to criterion for mixing similarity (Appendix B).

Future work in this area should be centered on evaluation of known flow fields with respect to their mixing efficiency. Helical flows, combined Poiseuille and Couette flows, axially symmetric swirling flows with uniform axial stretch, and vortex decay are likely candidates. It was shown that elongational flow is more efficient than shear flow. Real laminar mixers such as stirred tanks, screw extruders or various static mixers have more complex yet in principle analyzable flow fields.

PART II: DESCRIPTION OF MIXING OF IMMISCIBLE FLUIDS IN TERMS OF INTERMATERIAL AREA DENSITY

An exact description of the mixing of fluids is given by the location of material interfaces as functions of space and time. As demonstrated in Part I, knowledge of the motion provides such a description. However, this level of information is rare because velocity fields in mixing are complex. Other methods of analysis must be pursued.

Here we present an approach based on volume averages of quantities which measure the degree of mixing. Details are lost as a consequence of such a procedure, but the relationship with mixing experiments is simpler. The analysis gives insight to systems where knowledge of motion is incomplete and where only information of external macroscopic parameters is available, e.g., power input to a stirred tank.

Analysis is based on a hypothesis concerning the geometry of the mixture: *the lamellar structure assumption*. Introduction of different constitutive equations presents no problems to the analysis which is cast first in its most general form. However, assumptions of immiscibility or clearly defined interfaces, incompressibility, negligible interfacial surface tension, and topological motion are retained. It will be shown how numerical estimates of an efficiency index for mixing can be eventually evaluated with the aid of experimental measurements on the macroscopic system. Application to experimental data for viscous mixing in stirred tanks is given by Ottino and Macosko (1980).

Lamellar Structure Assumption

The word "lamellar" is used in this work with a different meaning than that of the properties of a velocity field, e.g. Complex Lamellar, Solenoid Complex Lamellar (see for example Aris, 1962, p. 64).

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 Kwon (1976), Ranz (1979) and Ottino et al. (1979). If $V_{\underset{\sim}{X}}$ denotes a simply connected volume enclosing a designated particle $\underset{\sim}{X}$, the mean value of intermaterial area density in $V_{\underset{\sim}{X}}$ is defined as:

$$\langle a_v \rangle_{V_{\underset{\sim}{X}}} \equiv \frac{\text{interfacial area between fluids in } V_{\underset{\sim}{X}}}{\text{volume of } V_{\underset{\sim}{X}}} \tag{58}$$

Extending the continuum hypothesis to a structured continuum, intermaterial area at point $\underset{\sim}{X}$ and time t is defined by:

$$a_v(\underset{\sim}{X}, t) \equiv \lim_{V_{\underset{\sim}{X}} \to 0} \langle a_v \rangle_{V_{\underset{\sim}{X}}} \tag{59}$$

In what follows $a_v(\underset{\sim}{X}, t)$ is assumed to be a smooth function of space and time.

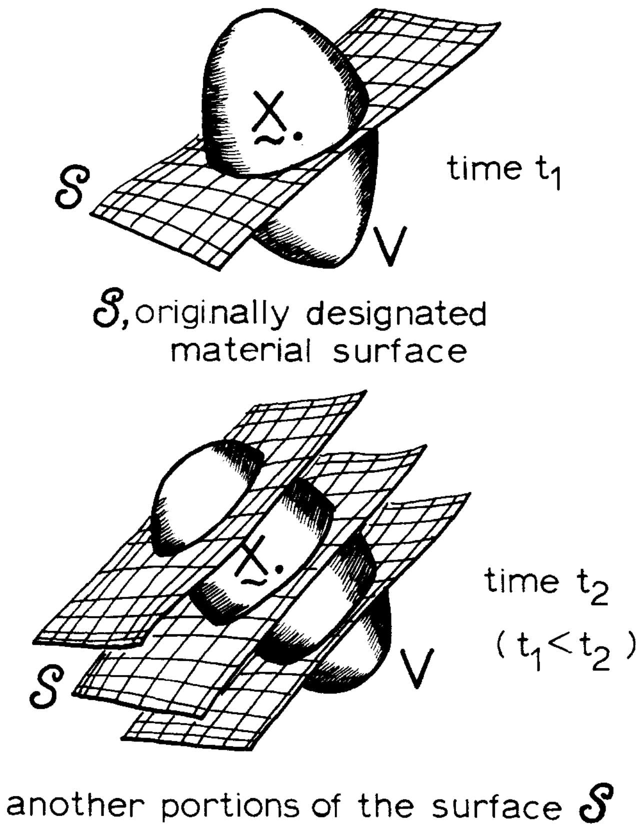

Figure 5. Pictorial representation of the formation of lamellar structures.

An equivalent measure of state of mixing, striation thickness, s, first proposed by Mohr et al. (1957), is defined by:

$$s \equiv 1/a_v \tag{60}$$

[Both a_v and s have physical meaning, but may have different uses. An average value of a_v is a clearly defined continuum quantity which measures state of mixing. Striation thickness, s, as defined here, is an equivalent measure and is a particular average of actual striation thickness (in the sense defined by Ottino et al. 1979). If molecular diffusion occurs and one wants to follow this process in detail, it is also necessary to recognize that s has distributed values and that deviation from average value may be of as much importance to the diffusional process as the average value. Here one considers a continuum quantity representing a single physical concept with some appropriate average value. (The problem of distribution of striation thickness is discussed by Ottino, 1980).]

Large values of a_v or small values of s imply a fine subdivision of the fluids. High volumetric average values of intermaterial area density are to be interpreted as good mixing. Supplementary discussion and references on lamellar structures are given in Ottino et al. (1979).

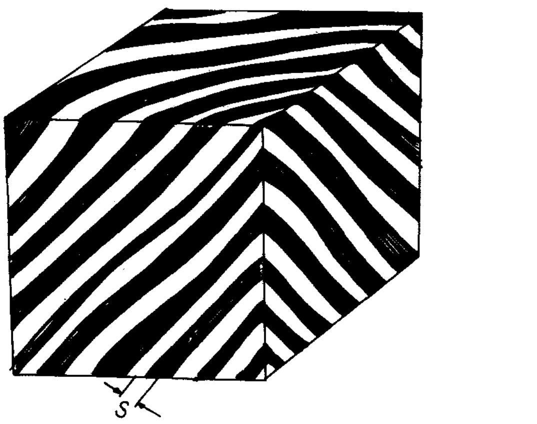

Figure 6. Instantaneous sectioning of a lamellar structure.

Consider the consequence of negligible interfacial tension between fluids on mixing topology. In the absence of interfacial tension, originally connected material fluid volumes remain connected throughout time. Topological features of surfaces and volumes are unchanged during the motion. In particular one fluid cannot form drops inside another.

Under such conditions we postulate that mixing will form a lamellar structure. This concept can be visualized in the following way. Consider a particle $\underset{\sim}{X}$ belonging to a material surface surrounded by an imaginary topological sphere of fixed volume V. As motion proceeds more and more material surface area is created and eventually another portion of the same surface will appear inside V (Figure 5). If mixing is effective, in the sense of distributing material surfaces homogeneously throughout the motion space, the normal distances between material surfaces will, on the average, decrease with time. In particular, due to the assumption of topological motion, two surfaces cannot collide and a surface cannot be divided in two. An instantaneous sectioning of a lamellar structure presents the appearance shown in Figure 6.

We want now to extend the meaning of the term $\underline{\underline{D}}:\hat{n}\hat{n}$ that gives the local rate of stretching η, of small material planes (Eq. 14 with $div\ \underset{\sim}{v} = 0$).

$$\frac{\dot{\eta}}{\eta} = -\underline{\underline{D}}:\hat{n}\hat{n} \tag{61}$$

Parallel material planes where $\hat{n}$ is the same for all surfaces under the same deformation tensor (given by a particular value of $\underline{\underline{D}}$) will experience the same stretching. Under such conditions intermaterial area density a_v is proportional to the area stretch, η. We write $a_v(\underset{\sim}{X}, t) = a_v(\underset{\sim}{X}, 0)\eta$ where zero time is some appropriate time.

There exists a space scale region below which a material plane cannot be folded. In this scale a small material plane remains planar during motion. In particular, at these scales, two small initially parallel small planes remain parallel (Ottino et al., 1979). This region associated with every particle $\underset{\sim}{X}$ of the fluid is denoted by $\&_X$. Given any flow field a small region of nearly uniform stretching action $\underline{\underline{D}}$ (region $\&_X$) can be defined by:

$$\int_{\partial\&_X} \bar{\underset{\sim}{v}} \cdot \bar{\underset{\sim}{\tau}}\, ds - \int_{\&_X} \bar{\underline{\underline{T}}}:\bar{\underline{\underline{D}}}\, dv = O(|\underset{\sim}{x}|^4) \tag{62}$$

where $\bar{\underset{\sim}{\tau}} = \bar{\underline{\underline{T}}} \cdot \hat{n}$ and overbars refer to quantities calculated in a frame $\bar{F}$ moving with particle $\underset{\sim}{X}$. Eq. 22 expresses the criterion that in this region viscous work is consumed as viscous dissipation. Length $|\underset{\sim}{x}|$ denotes the size of region $\&_X$. Appendix C gives a more detailed discussion of flow in the region $\&_X$.

Thus, conceptually a material point in the fluid is assigned a value of intermaterial area per unit volume and a small region of stretching, $\&_X$. In any region $\&_X$ intermaterial area generation is given by:

$$\overline{ln\ a_v(\underset{\sim}{X}, t)} = -\underline{\underline{D}}:\hat{n}\hat{n} \tag{63}$$

which can also be written as:

$$\frac{\partial\ ln\ a_v(\underset{\sim}{X}, t)}{\partial t} + \underset{\sim}{v} \cdot grad(ln\ a_v(\underset{\sim}{x}, t)) = -\underline{\underline{D}}:\hat{n}\hat{n} \tag{64}$$

Eq. 64 is a transport equation for property a_v. [It should be stressed that one cannot obtain the $a_v(\underset{\sim}{x}, t)$ field by solving Eq. 69 with some initial and boundary conditions. The solution implies knowledge of $\underline{\underline{D}}:\hat{n}\hat{n}$ which in turn implies knowledge of the whole motion, i.e., the mapping of all interfaces in space and time. Unfortunately, Eq. 70 cannot be solved with only the knowledge of the velocity field.] Under smoothness assumptions on a_v, Eq. 64 can be integrated for macroscopic systems to obtain volumetric efficiency average information as shown in the following section.

The local value of intermaterial area generation $-\underline{\underline{D}}:\hat{n}\hat{n}$, is bounded according to Cauchy-Schwarz's inequality, by $(\underline{\underline{D}}:\underline{\underline{D}})^{1/2}$. An efficiency index of mixing $e = e(\underline{x}, t)$ is defined by:

$$e = \frac{-\underline{\underline{D}}:\hat{n}\hat{n}}{(\underline{\underline{D}}:\underline{\underline{D}})^{1/2}} \tag{65}$$

Accordingly, Eq. 64 is written as:

$$\frac{\partial\, ln\, a_r}{\partial t} + \underline{v} \cdot grad(ln\, a_r) = e(\underline{x}, t)\, (\underline{\underline{D}}:\underline{\underline{D}})^{1/2} \tag{66}$$

Knowledge of the velocity field permits evaluation of $(\underline{\underline{D}}:\underline{\underline{D}})^{1/2}$. We have, however, replaced a term of difficult calculation, $-\underline{\underline{D}}:\hat{n}\hat{n}$, by a similar one, $e(\underline{x}, t)$. However, $e(\underline{x}, t)$ has a physical meaning, and its numerical value provides a measure of the effectiveness of mixing flows.

The physical meaning of $e(\underline{x}, t)$ is made clearer if it is written for a Newtonian fluid as:

$$e = \frac{-\underline{\underline{D}}:\hat{n}\hat{n}}{\sqrt{\dfrac{\epsilon}{2\mu}}} \tag{67}$$

where ϵ is the so-called viscous dissipation per unit volume per unit time ($\epsilon = 2\mu\underline{\underline{D}}:\underline{\underline{D}}$). Meanings for other constitutive equations will be made evident at the end of this Section. Eq. 67 can be interpreted as a ratio of energy used to create intermaterial area with respect to energy dissipated at a particular point.

Consider now integral formulas which can be developed for two systems of engineering interest, closed constant-volume systems (e.g., stirred tanks) and open flow systems (e.g., static mixers and screw extruders, Middleman 1977). Representation of these two systems is shown in Figure 7a,b.

For systems of constant volume integration of Eq. 66 over volume V (Figure 7a) leads to:

$$\frac{d\, \overline{\overline{ln\, a_r}}}{dt} = \overline{\dot{\overline{ln\, a_r(\underline{x}, t)}}} = \overline{e(x, t)\, (\underline{\underline{D}}:\underline{\underline{D}})^{1/2}} \tag{68}$$

where the mean value of any function $f(x, t)$ is defined by:

$$\overline{\overline{f}} = \frac{\int_V f\, dv}{\int_V dv} \tag{69}$$

on a material volume V.

Equation 68 is proved by using the relation valid for incompressible fluids:

$$\int_V \dot{\overline{ln\, a_r}} dv = \dot{\overline{\int_V ln\, a_r dv}} \tag{70}$$

(Serrin, 1960, p. 133). Eq. 66 is now integrated for a general flow system such as the one represented in Figure 7b. We require that the normal velocity component of the velocity $\underline{v}$ to the boundary ∂V be zero, i.e., $\underline{v}|_{\partial V} \cdot \hat{t} = 0$. This condition is satisfied in most common mixing systems with moving boundaries, for example, screw extruders. We define a gradient operation ∇_A over the cross-sectional areas, such that $\nabla(\cdot) = \nabla_A(\cdot) + \partial(\cdot)\hat{n}/\partial n$. Eq. 66 is rewritten as:

$$\frac{\partial\, ln\, a_r}{\partial t} + \underline{v} \cdot \nabla_A\, ln\, a_r + v_n \frac{\partial\, ln\, a_r}{\partial n} = e(\underline{x}, t)\, (\underline{\underline{D}}:\underline{\underline{D}})^{1/2} \tag{71}$$

For steady flows of incompressible fluid, Eq. 71 reduces to:

$$\nabla_A \cdot (\underline{v}\, ln\, a_r) + \frac{\partial}{\partial n}(v_n\, ln\, a_r) = e(\underline{x}, t)\, (\underline{\underline{D}}:\underline{\underline{D}})^{1/2} \tag{72}$$

since $\underline{v} \cdot \nabla_A\, ln\, a_r = \nabla_A \cdot (\underline{v}\, ln\, a_r) - (\nabla_A \cdot \underline{v})\, ln\, a_r$, $\nabla_A \cdot \underline{v} = -\partial v_n/\partial n$ and $\int_A \nabla_A \cdot (\underline{v}\, ln\, a_r) dA = 0$ by the condition $\underline{v}|_{\partial V} \cdot \hat{t} = 0$.

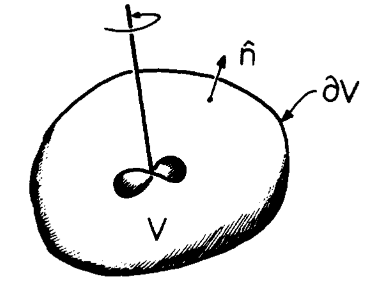

Figure 7a. Representation of a closed volume mixer.

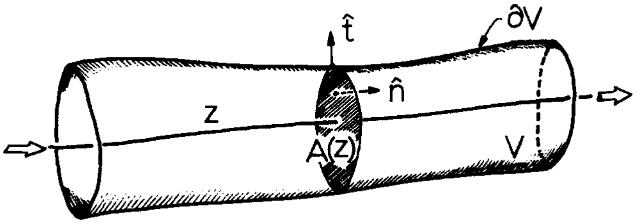

Figure 7b. Representation of a continuous flow mixer.

Integration of Eq. 72 over the cross sectional area yields:

$$\frac{d}{dn} \int_A v_n\, ln\, a_r dA = \int_A e(\underline{x}, t)\, (\underline{\underline{D}}:\underline{\underline{D}})^{1/2} dA$$

and

$$\frac{d}{dn} \langle\langle ln\, a_r \rangle\rangle = \frac{\overline{e(\underline{x}, t)\, (\underline{\underline{D}}:\underline{\underline{D}})^{1/2}}}{\bar{v}_n} \tag{73}$$

where mean values of any function f are defined by:

$$\langle\langle f \rangle\rangle = \frac{\int_A f v_n dA}{\int_A v_n dA} \text{ and } \overline{f} = \frac{\int_A f dA}{\int_A dA} \tag{74}$$

In terms of a curvilinear coordinate z, everywhere tangential to the vectors $\hat{n}$, that is, there exists a 1-1 correspondence between $\hat{n}$ and z, we obtain:

$$\frac{d}{dz} \langle\langle ln\, a_r \rangle\rangle = \frac{\overline{e(\underline{x}, t)\, (\underline{\underline{D}}:\underline{\underline{D}})^{1/2}}}{\bar{v}_z} \tag{75}$$

Maximum production of intermaterial area is given by:

constant-volume systems
$$\overline{\overline{\dot{ln\, a_r}}} \le \overline{\overline{(\underline{\underline{D}}:\underline{\underline{D}})^{1/2}}} \tag{76}$$

and

continuous flow systems
$$\frac{d}{dz} \langle\langle ln\, a_r \rangle\rangle \le \frac{\overline{(\underline{\underline{D}}:\underline{\underline{D}})^{1/2}}}{\bar{v}_z} \tag{77}$$

since $e(\underline{x}, t) \le 1$.

We will now put differential inequalities (Eqs. 76 and 77) in a more appropriate form for practical calculations. To remove power ½ outside mean values we use the Hölder inequality (Eq. 19):

constant-volume systems
$$\overline{\overline{\dot{ln\, a_r}}} \le (\overline{\overline{\underline{\underline{D}}:\underline{\underline{D}}}})^{1/2} \tag{78}$$

continuous flow systems
$$\frac{d}{dz} \langle\langle ln\, a_r \rangle\rangle \le \frac{(\overline{\underline{\underline{D}}:\underline{\underline{D}}})^{1/2}}{\bar{v}_z} \tag{79}$$

The right hand side of these inequalities are relatively easy to calculate in a known flow field and represent limits to the mixing capacity of macroscopic systems.

An alternative way of writing the right hand sides of Eqs. 76 and 79 and highlight the role of vorticity in mixing is to make use of the Bobyleff-Forsythe formula (Serrin, 1960, p. 250), valid for Newtonian incompressible fluids.

$$2\int_V \underline{\underline{D}}:\underline{\underline{D}}\, dv = \int_V \omega^2 dv + 2\oint_{\partial V} \dot{\underline{v}} \cdot \hat{n}\, da \tag{80}$$

where $\omega = |\underline{\omega}| = |rot\ \underline{v}|$, and V is a finite fixed in space region with boundary surface ∂V. Thus, for example, in a steady flow of a constant cross sectional area of a continuous flow system,

$$\overline{\overline{\underline{\underline{D}}:\underline{\underline{D}}}} = \overline{\overline{\omega^2}}/2$$

Terms $\overline{\overline{\underline{\underline{D}}:\underline{\underline{D}}}}$ and $\overline{\underline{\underline{D}}:\underline{\underline{D}}}$ are related simply to $\underline{\underline{\tau}}:\underline{\underline{D}}$ for some constitutive equations. Values $\underline{\underline{\tau}}:\underline{\underline{D}}$ and $\underline{\underline{\tau}}:\underline{\underline{D}}$ can be obtained from macroscopic balances or experimental measurements. They are related to external parameters, e.g., impeller power, pressure gradients, etc.

The following relations hold for Newtonian and Power Law fluids:

Fluid

Newtonian Fluid $\underline{\underline{\tau}} = 2\mu\underline{\underline{D}},\ \underline{\underline{D}}:\underline{\underline{D}} = \dfrac{\underline{\underline{\tau}}:\underline{\underline{D}}}{2\mu}$

Power Law Fluid $\underline{\underline{\tau}} = 2\eta|\sqrt{2\underline{\underline{D}}:\underline{\underline{D}}}|^{n-1}\underline{\underline{D}},\ \underline{\underline{D}}:\underline{\underline{D}} = \dfrac{1}{2}\left(\dfrac{\underline{\underline{\tau}}:\underline{\underline{D}}}{\eta}\right)^{2/n+1}$

Thus, for these fluids, measures of $\overline{\overline{\underline{\underline{\tau}}:\underline{\underline{D}}}}$ and $\overline{\underline{\underline{\tau}}:\underline{\underline{D}}}$ provide knowledge of $\underline{\underline{D}}:\underline{\underline{D}}$ and $\underline{\underline{D}}:\underline{\underline{D}}$.

When other constitutive equations hold, the relationship is not trivial as shown by the following examples:

Fluid	Constitutive Equation	
Ellis Fluid	$\underline{\underline{\tau}} = \dfrac{2\mu}{1 + m(\underline{\underline{D}}:\underline{\underline{D}})^{n-1/2}}$	$\underline{\underline{\tau}}:\underline{\underline{D}} = \dfrac{2\mu\underline{\underline{D}}:\underline{\underline{D}}}{1 + m(\underline{\underline{D}}:\underline{\underline{D}})^{n-1/2}}$
Reiner-Rivlin Fluid (Serrin, 1960, p. 235)	$\underline{\underline{\tau}} = \alpha_1\underline{\underline{D}} + \alpha_2\underline{\underline{D}} \cdot \underline{\underline{D}}$	$\underline{\underline{\tau}}:\underline{\underline{D}} = \alpha_1\underline{\underline{D}}:\underline{\underline{D}} + \alpha_2\underline{\underline{D}} \cdot \underline{\underline{D}}:\underline{\underline{D}}$

The following difficulties arise:

Ellis Fluid $\dfrac{\underline{\underline{\tau}}:\underline{\underline{D}}}{2\mu} > \underline{\underline{D}}:\underline{\underline{D}}$ if $m < 0$

$\dfrac{\underline{\underline{\tau}}:\underline{\underline{D}}}{2\mu} < \underline{\underline{D}}:\underline{\underline{D}}$ if $m > 0$

Only in case $m < 0$ do we have a bound for the bound of Eqs. 78 and 79.

For the Reiner-Rivlin fluid the difficulty with the bounds is interesting from a theoretical point of view. $\underline{\underline{\tau}}:\underline{\underline{D}}$ can be either smaller or larger than $\alpha_1\underline{\underline{D}}:\underline{\underline{D}}$ depending on the sign of $\alpha_2\underline{\underline{D}} \cdot \underline{\underline{D}}:\underline{\underline{D}}$. For elongational flows for example, $\alpha_2\underline{\underline{D}} \cdot \underline{\underline{D}}:\underline{\underline{D}}$ can be arbitrarily made positive or negative depending on the sign of α_2 by an appropriate choice of $\dot{\epsilon}$ (positive for a diverging elongation, negative for contracting). Coefficient $\dot{\epsilon}$ is usually referred to as an extensional parameter. $\underline{\underline{D}}:\underline{\underline{D}}$ is not simply bounded by $\underline{\underline{\tau}}:\underline{\underline{D}}$. Research is needed for application of mixing bounds to viscoelastic fluids, contributions of energy dissipated and energy stored, and the interpretation of spontaneous demixing.

Average Efficiency Index of Mixing

There is no conceptual difficulty in defining an average value of the efficiency index for mixing by:

closed systems

$$\overline{\overline{eff(t)}} = \frac{\overline{\overline{e(\underline{x}, t)\ (\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}}}{\overline{\overline{(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}}} \tag{81}$$

continuous flow systems

$$\overline{eff(z)} = \frac{\overline{e(\underline{x}, t)\ (\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}}{\overline{(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}} \tag{82}$$

[Alternatively average efficiencies might be defined as:

$$\overline{\overline{eff(t)^*}} = \frac{\overline{\overline{e(\underline{x}, t)\ (\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}}}{\overline{\overline{(\underline{\underline{D}}:\underline{\underline{D}})}}^{\frac{1}{2}}}$$

$$\overline{eff(z)^*} = \frac{\overline{e(\underline{x}, t)\ (\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}}{\overline{(\underline{\underline{D}}:\underline{\underline{D}})}^{\frac{1}{2}}}$$

By virtue of Hölder inequality $\overline{\overline{(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}} \leq \overline{\overline{(\underline{\underline{D}}:\underline{\underline{D}})}}^{\frac{1}{2}}$, $\overline{(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}} \leq \overline{(\underline{\underline{D}}:\underline{\underline{D}})}^{\frac{1}{2}}$ we have $\overline{\overline{eff(t)}} \leq \overline{\overline{eff(t)^*}}$ and $\overline{eff(z)} \leq \overline{eff(z)^*}$. As indicated, $eff(t)$ is only a function of time and $eff(z)$ is only a function of coordinate z. Thus Eqs. 68 and 75 are written as:

$$\overline{\overline{\dot{ln\ a_v}}} = \overline{\overline{eff(t)}}\ \overline{\overline{(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}} \tag{83}$$

$$\frac{d}{dz}\langle\langle ln\ a_v\rangle\rangle = \frac{\overline{eff(z)}\ \overline{(\underline{\underline{D}}:\underline{\underline{D}})^{\frac{1}{2}}}}{\bar{v}_n} \tag{84}$$

Eq. 83 has been used to determine average efficiency index for batch reactors based on experimental data of power consumption to achieve some degree of homogeneity (Ottino and Macosko, 1980). Applications for static mixers; single screw extruders, and pipe flow are underway.

From a practical point of view one should know the relation among $\overline{\overline{ln\ a_v}}$ and $ln\ \overline{\overline{a_v}}$, $\langle\langle ln\ a_v\rangle\rangle$ and $ln\langle\langle a_v\rangle\rangle$ since $\overline{\overline{a_v}}$ and $\langle\langle a_v\rangle\rangle$ are probably accessible from experimental information. The relation is provided by the Jensen inequality (Eq. 20).

$$ln\ \overline{\overline{a_v}} \geq \overline{\overline{ln\ a_v}} \tag{85}$$

$$ln\ \langle\langle a_v\rangle\rangle \geq \langle\langle ln\ a_v\rangle\rangle \tag{86}$$

Conclusions

This paper presents a mathematical foundation for a process often claimed to be understood only in a qualitative sense. However, it is in the fundamental concepts, physical in origin, where the quantitative basis rests. Thus the novelty resides in a correct, tractable, qualitative picture.

Mixing was described in terms of intermaterial area density, a quantity that should be accessible from an experimental point of view. Discussion of the structures produced by continuous deformation of materials in topological motions led to a lamellar structure assumption and equations governing the behavior of intermaterial area density in closed and continuous flow systems. Average values of an efficiency index for mixing were provided and its relation to experimental measurements was outlined.

Although attaining the goal of a full understanding of mixing processes lies in the future, this treatment should provide a rational setting for further developments.

We should recognize that important physical situations are not included in this simplified theory. The most important are:

(i) Mass transfer between materials
(ii) Simultaneous mass transfer and reaction
(iii) Presence of interfacial surface tension.

This list is in the order of increasing mathematical complexity. Eventually, the theory should be expanded to include these phenomena some of which have been studied outside the scope of mixing theory. We treat (i) and (ii) elsewhere (Ottino, 1979, 1980).

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APPENDIX A: CONTINUUM MECHANICS FORMULATIONS

Deformation of an elementary material length

With reference to Figure 1a we define lineal stretching λ as:

$$\lambda \equiv \frac{|d\underline{x}|}{|d\underline{X}|} \tag{A1}$$

Since $d\underline{x} = \underline{\underline{F}} \cdot d\underline{X}$, computation of λ^2 yields:

$$\lambda^2 \equiv \frac{(\underline{\underline{F}} \cdot d\underline{X}) \cdot (\underline{\underline{F}} \cdot d\underline{X})}{|dX|^2} \tag{A2}$$

Eq. A2 can also be written as:

$$\boxed{\lambda^2 = \underline{\underline{C}}:\hat{M}\hat{M}} \quad \text{(corresponds to Eq. 4)}$$

where $\hat{M} = d\underline{X}/|d\underline{X}|$ and $\underline{\underline{C}} = \underline{\underline{F}}^T \cdot \underline{\underline{F}}$ is the Cauchy-Green strain tensor since

$$(\underline{\underline{F}} \cdot d\underline{X}) \cdot (\underline{\underline{F}} \cdot d\underline{X}) = \underline{\underline{F}}^T \cdot \underline{\underline{F}}:d\underline{X}d\underline{X}$$

Replacing this last result in Eq. A2 and taking the material derivative of λ

$$2\lambda\dot{\lambda} = (\dot{\underline{\underline{F}}}^T\underline{\underline{F}} + \underline{\underline{F}}^T\dot{\underline{\underline{F}}}): \frac{d\underline{X}\ d\underline{X}}{|d\underline{X}|^2} \tag{A3}$$

but $\dot{\underline{\underline{F}}} = (grad\ \underline{v}) \cdot \underline{\underline{F}}$. Then $(\dot{\underline{\underline{F}}})^T = \underline{\underline{F}}^T \cdot (grad\ \underline{v})^T$ (A4)

Consequently,

$$2\lambda\dot{\lambda} = [\underline{\underline{F}}^T \cdot (grad\ \underline{v})^T \cdot \underline{\underline{F}} + \underline{\underline{F}}^T \cdot (grad\ \underline{v}) \cdot \underline{\underline{F}}]: \frac{d\underline{X}\ d\underline{X}}{|d\underline{X}|^2} \tag{A5}$$

$$2\lambda\dot{\lambda} = \underline{\underline{F}}^T \cdot 2\underline{\underline{D}} \cdot \underline{\underline{F}}: \frac{d\underline{X}\ d\underline{X}}{|d\underline{X}|^2} \tag{A6}$$

$$\lambda\dot{\lambda} = \underline{\underline{F}}^T \cdot \underline{\underline{D}}: \frac{d\underline{x}\ d\underline{X}}{|d\underline{X}|^2} \tag{A7}$$

but

$$\underline{\underline{F}}^T \cdot \underline{\underline{D}}: d\underline{x}\ d\underline{X} = [\underline{\underline{D}} \cdot d\underline{x}] \cdot [\underline{\underline{F}} \cdot d\underline{X}] = \underline{\underline{D}}: d\underline{x}\ d\underline{x} \tag{A8}$$

Then replacing Eq. A8 in Eq. A7 and multiplying and dividing by $|d\underline{x}|^2$:

$$\lambda\dot{\lambda} = \frac{\underline{\underline{D}}: d\underline{x}\ d\underline{x}}{d\underline{X}^2}\ \frac{|d\underline{x}|^2}{|d\underline{x}|^2} \tag{A9}$$

Using $\hat{m} \equiv \dfrac{d\underline{x}}{|d\underline{x}|}$ and $\lambda \equiv \dfrac{d\underline{x}}{|d\underline{X}|}$

we obtain $\boxed{\dfrac{\dot{\lambda}}{\lambda} = \underline{\underline{D}}:\hat{m}\hat{m}}$ (corresponds to Eq. 13) (A10)

Change of $\hat{m}$ as function of the motion and time

By definition

$$\hat{m} = \frac{d\underline{x}}{|d\underline{x}|} = \frac{\underline{\underline{F}} \cdot d\underline{X}}{|d\underline{x}|}\ \frac{|d\underline{X}|}{|d\underline{X}|} = \frac{\underline{\underline{F}} \cdot \hat{M}}{\lambda} \tag{A11}$$

(corresponds to Eq. 5)

Computation of $\hat{m}$ yields

$$\dot{\hat{m}} = \frac{(grad\ \underline{v}) \cdot \underline{\underline{F}} \cdot \hat{N}}{\lambda} - (\underline{\underline{D}}:\hat{m}\hat{m})\hat{m} \tag{A12}$$

Rearrangement of Eq. A12 gives:

$$\boxed{\dot{\hat{m}} = (\underline{\underline{D}} + \underline{\underline{\Omega}}) \cdot \hat{m} - (\underline{\underline{D}}:\hat{m}\hat{m})\hat{m}} \tag{A13}$$

(corresponds to Eq. 9)

Deformation of an elementary material plane

With reference to Figure 1b we define:

$$d\underline{A} = d\underline{X}_1 \times d\underline{X}_2 = \hat{N}dA \qquad d\underline{a} = d\underline{x}_1 \times d\underline{x}_2 = \hat{n}da \tag{A14}$$

$$dA = |d\underline{A}| \qquad da = |d\underline{a}| \tag{A15}$$

and

$$\eta = \frac{|d\underline{a}|}{|d\underline{A}|} \tag{A16}$$

Making use of (Nanson's formula, Malvern, 1969 p. 169)

$$d\underline{a} = (det\ \underline{\underline{F}})\ (\underline{\underline{F}}^{-1})^T \cdot d\underline{A} \tag{A17}$$

Computation of η^2 yields:

$$\eta^2 = \frac{[(det\ \underline{\underline{F}})\ (\underline{\underline{F}}^{-1})^T \cdot d\underline{A}] \cdot [(det\ \underline{\underline{F}})\ (\underline{\underline{F}}^{-1})^T \cdot d\underline{A}]}{|d\underline{A}| \cdot |d\underline{A}|}$$

$$= (det\ \underline{\underline{F}})^2\ (\underline{\underline{F}}^{-1}) \cdot (\underline{\underline{F}}^{-1})^T: \frac{d\underline{A}\ d\underline{A}}{|d\underline{A}|^2} \tag{A18}$$

Defining $\underline{\underline{C}} = \underline{\underline{F}}^T \cdot \underline{\underline{F}}$, Eq. A18 can be written as:

$$\boxed{\eta^2 = (det\ \underline{\underline{F}})^2\ \underline{\underline{C}}^{-1}:\hat{N}\hat{N}} \quad \text{(corresponds to Eq. 7)} \tag{A19}$$

Taking the material derivative of η,

$$\dot{\eta} = \overline{(det\ \underline{\underline{F}})}^{\cdot}\ (\underline{\underline{C}}^{-1}:\hat{N}\hat{N})^{\frac{1}{2}} + \frac{(det\ \underline{\underline{F}})}{2}\ (\underline{\underline{C}}^{-1}:\hat{N}\hat{N})^{-\frac{1}{2}}\ \overline{\underline{\underline{C}}^{-1}}^{\cdot}:\hat{N}\hat{N} \tag{A20}$$

Making use of

(i) $\overline{(det\ \underline{\underline{F}})}^{\cdot} = (det\ \underline{\underline{F}})\ div\ \underline{v}$ (A21)

(ii) $\overline{\underline{\underline{C}}^{-1}}^{\cdot} = -\underline{\underline{C}}^{-1} \cdot \dot{\underline{\underline{C}}} \cdot \underline{\underline{C}}^{-1}$ (A22)

(iii) $\dot{\underline{\underline{C}}} = 2\underline{\underline{F}}^T \cdot \underline{\underline{D}} \cdot \underline{\underline{F}}$ (A23)

we obtain for Eq. A20:

$$\dot{\eta} = (div\ \underline{v})\eta - \frac{(det\ \underline{\underline{F}})}{\sqrt{\underline{\underline{C}}^{-1}:\hat{N}\hat{N}}}\underline{\underline{F}}^{-1} \cdot \underline{\underline{D}} \cdot (\underline{\underline{F}}^{-1})^T:\hat{N}\hat{N} \tag{A24}$$

In terms of Eq. A17, $\hat{n}$ can be written as:

$$\hat{n} = (det\ \underline{\underline{F}})\ (\underline{\underline{F}}^{-1})^T \cdot \frac{d\underline{A}}{|d\underline{A}|}\ \frac{|d\underline{A}|}{|d\underline{a}|} = \frac{(det\ \underline{\underline{F}})\ (\underline{\underline{F}}^{-1})^T \cdot \hat{N}}{\eta} \tag{A25}$$

(corresponds to Eq. 8)

Since the last terms of the right hand side of Eq. A29 can be shown to be,

$$\frac{(det\ \underline{\underline{F}}) \cdot (\underline{\underline{F}}^{-1}) \cdot \underline{\underline{D}} \cdot (\underline{\underline{F}}^{-1})^T:\hat{N}\hat{N}}{\sqrt{\underline{\underline{C}}^{-1}:\hat{N}\hat{N}}} = (\underline{\underline{D}}:\hat{n}\hat{n})\eta \tag{A26}$$

then

$$\boxed{\frac{\dot{\eta}}{\eta} = div\ \underline{v} - \underline{\underline{D}}:\hat{n}\hat{n}} \tag{A27}$$

(corresponds to Eq. 14)

APPENDIX B: SIMILARITY AND MIXING

This Appendix briefly analyzes the implications of geometrical and dynamical similarity (Batchelor, 1967; Bird et al., 1960) in mixing problems. The objective is to form clear ideas with regard to effects of change of scale in mixing processes. Consider two systems: A, A′ (either closed on continuous) geometrically similar, i.e., both geometries are related by a constant multiplicative factor. System A is composed of two fluids a and b mixed by a motion χ_A, whereas System A′ is composed of fluids a', b' mixed by motion $\chi_{A'}$. Consider first when motions χ_A and $\chi_{A'}$ are similar. By similar we mean equal reduced expressions. A reduced expression is one in which all variables are cast in nondimensional form. A nondimensional variable has the general form:

$$\text{reduced variable}^* = \frac{\text{variable}}{\text{characteristic value for the variable}}$$

Assume that a choice of characteristic values for Systems A and A′ has been made (i.e., L_A, L'_A, characteristic lengths, T_A, T'_A, characteristic times, etc., for Systems A and A′). The objective is to determine under what conditions the two reduced motions:

$$\underset{\sim}{x}^*_A = \chi^*_A(\underset{\sim}{X}^*_A, t^*_A) \text{ and } \underset{\sim}{x}^*_{A'} = \chi^*_{A'}(\underset{\sim}{X}^*_{A'}, t^*_{A'})$$

are equal. If this holds it follows that reduced velocity fields, reduced stretching tensor fields, etc., are also equal. Subsequent discussion is restricted to incompressible pairs of Newtonian fluids a, b and a', b' without interfacial tension. Interfacial conditions separating fluids a, b and a', b' in contact at interfaces of Systems A and A′ require that:

System A Continuity of Velocity

$$\underset{\sim}{v}^*_{Aa} = \underset{\sim}{v}^*_{Ab}$$

Equality of Stresses — On Contact Interfaces of System A (B1)

$$2\mu_a \underset{\approx}{D}^*_{Aa} = 2\mu_b \underset{\approx}{D}^*_{Ab}$$

System B Continuity of Velocity

$$v^*_{A'a'} = v^*_{A'b'}$$

Equality of Stresses — On Contact Interfaces of System A′ (B2)

$$2\mu_{a'} \underset{\approx}{D}^*_{A'a'} = 2\mu_{b'} \underset{\approx}{D}^*_{A'b'}$$

Since $\underset{\approx}{D}^*_{A'a'} = \underset{\approx}{D}^*_{Aa}$, $\underset{\approx}{D}^*_{A'b'} = \underset{\approx}{D}^*_{Ab}$ from Eqs. B1 and B2:

$$\frac{\mu_a}{\mu_{a'}} = \frac{\mu_b}{\mu_{b'}} \tag{B3}$$

appears as criterion.

A standard nondimensionalization process of the Navier-Stokes equation for equality of reduced velocity descriptions of fluid a in motion A and fluid a' in motion A′ requires:

$$Re_{Aa} = Re_{A'a'} \tag{B4}$$

[For simplicity, a Froude number is not considered.] Similarly for fluids b, b' in motions χ_A and $\chi_{A'}$

$$Re_{Ab} = Re_{A'b'} \tag{B5}$$

From Eqs. B3, B4 and B5,

$$\frac{\rho_{a'}}{\rho_a} = \frac{\rho_{b'}}{\rho_b} \tag{B6}$$

appears as another criterion.

Under all the above conditions, nondimensional (reduced) differential equations (momentum and continuity equations) are equal. Since by hypothesis reduced initial and boundary conditions are equal, their solutions, e.g., reduced velocity fields, are also equal. Reduced motions, integral solutions of velocity fields, are therefore identical.

Systems A and A′ with equal reduced motions χ^*_A, $\chi^*_{A'}$ produce equal (relative deformations of lines and surfaces, in particular interfaces, with equal reduced initial conditions. This can be proved by the fact that deformations are dimensionless. It is also clear that mixing efficiencies as defined for stretching of lines and areas are also equal when compared for equation reduced fluid particles and times. Consider for example length deformation given by Eq. 4:

$$\lambda(\underset{\sim}{X}, t) = \sqrt{(\nabla\chi)^T \cdot (\nabla\chi):\hat{N}\hat{N}} \tag{B7}$$

We can then write:

$$\lambda_A(\underset{\sim}{X}^*_A, t^*_A) = \sqrt{(\nabla^*_A\chi_A)^T \cdot (\nabla^*_A\chi_A):\hat{N}_A\hat{N}_A} \tag{B8}$$

and

$$\lambda_{A'}(\underset{\sim}{X}^*_A, t^*_{A'}) = \sqrt{(\nabla^*_{A'}\chi_{A'})^T \cdot (\nabla^*_{A'}\chi_{A'}):\hat{N}_{A'}\hat{N}_{A'}}$$

which satisfy

$$\lambda_A(\underset{\sim}{X}^*_A, t^*_A) = \lambda_{A'}(\underset{\sim}{X}^*_{A'}, t^*_{A'})$$

if

$$\underset{\sim}{X}^*_A = \underset{\sim}{X}^*_{A'}, \text{ and } t^*_A = t^*_{A'}$$

In mixing absolute (as opposed to relative) values of areas, intermaterial area density and striation thickness are essential. Intermaterial areas of Systems A and A′ computed by Eq. 26 satisfy:

$$\frac{A_A(\{\hat{N}_A\}, t^*_A)}{L^2_A} = \frac{A_{A'}(\{\hat{N}_{A'}\}, t^*_{A'})}{L^2_{A'}} \tag{B9}$$

It is then clear that intermaterial area generated in geometrically similar closed systems with equal reduced initial and boundary conditions and equal reduced motions satisfy (by Eq. 65):

$$\overline{\overline{a_{v_A}(t^*_A)}}L_A = \overline{\overline{a_{v_{A'}}(t^*_{A'})}}L_{A'} \tag{B10}$$

Under the same conditions intermaterial area delivered at the exit of a continuous flow mixer satisfy

$$\langle\langle ln\ a_{v_A}(z_A)\rangle\rangle L_A = \langle\langle ln\ a_{v_{A'}}(z_{A'})\rangle\rangle L_{A'} \tag{B11}$$

which can be proved by Eq. B11 since efficiencies are equal under equal reduced conditions. These self-evident facts have practical implications. For example if closed System Mixer A empirically designed works successfully when $\overline{\overline{a_{v_A}}}$ has reached some unknown value for time t^*_A, mixer A′ geometrically and dynamically similar will work if $L_A > L_{A'}$ and $t^*_{A'} = t^*_A$ since:

$$\overline{\overline{a_{v_{A'}}(t^*_{A'})}} = \frac{L_A}{L_{A'}} \overline{\overline{a_{v_A}(t^*_A)}}$$

because

$$\overline{\overline{a_{v_{A'}}(t^*_{A'})}} > \overline{\overline{a_{v_A}(t^*_A)}}$$

It is then concluded that in mixer design safe scale-down criteria can be established.

APPENDIX C: FLOW AT SMALL SCALES

The expansion of the flow field in a moving plane $\bar{F}$ centered on the material particle $\underset{\sim}{X}$ at distance $\underset{\sim}{x}$ is:

$$\bar{\underset{\sim}{v}} = \overline{(grad\ \underset{\sim}{v})}_{\underset{\sim}{X}} \cdot \bar{\underset{\sim}{x}} + o(\bar{\underset{\sim}{x}}^2)$$

where overbars refer to quantities measured in frame $\bar{F}$ (in what follows overbars are omitted. Quantities are to be understood in the moving frame $\bar{F}$). If $\bar{F}$ is such that its axes are the axes of principal stretching we have

$$[(grad\ \underset{\sim}{v})_{\underset{\sim}{X}}]_{ij} = \begin{Bmatrix} D_{11} & 0 & 0 \\ 0 & D_{22} & 0 \\ 0 & 0 & D_{33} \end{Bmatrix} \quad D_{ii} = D_{ii}(\underset{\sim}{X}, t)$$

so the motion around $\underset{\sim}{X}$ is:

$$v_i = D_{ii}(\underset{\sim}{X}, t)x_i + o(x_i^2)$$

with $\sum_{i=1}^{3} D_{ii} = 0$ for incompressible fluids. For a small enough region $\&_{\underset{\sim}{X}}$, where second order terms are negligible, the flow is represented by:

$$v_i \approx D_{ii}(\underset{\sim}{X}, t)x_i \text{ in } \&_{\underset{\sim}{X}}$$

or an eliptically symmetrical stagnation flow, i.e., the flow is irrotational in $\bar{F}$. Our concern here is a characterization of the $\&_{\underset{\sim}{X}}$ region.

First note the following results:

(i) $div\ \underset{\approx}{\tau} = 0$, where $\underset{\approx}{\tau}$ is the viscous part of the stress tensor for a Newtonian incompressible fluid in a region of irrotational flow.

(ii) div $[\underset{\approx}{T} \cdot \underset{\sim}{v}] = \underset{\approx}{T}$: grad $\underset{\sim}{v}$ at small scales where $\underset{\approx}{T}$ is the stress tensor and $\underset{\sim}{v}$ is the relative velocity field with respect to $\underset{\sim}{X}$ if $div\ \underset{\approx}{T} = 0$ is bounded.

Proof of (i). If flow is irrotational $\underset{\sim}{v} = grad\ \phi$ where ϕ is the velocity potential (Batchelor, 1967, p. 110). For incompressible fluids $div\ \underset{\sim}{v} = \nabla^2\phi = 0$. For Newtonian fluids:

$$div\ \underset{\approx}{\tau} = div[\mu[grad\ \underset{\sim}{v} + (grad\ \underset{\sim}{v})^T]$$
$$= \mu div[grad(grad\ \phi) + [grad(grad\ \phi)]^T]$$

with $grad(grad\ \phi) = (grad(grad\ \phi))^T$, since $grad[\nabla^2\phi] = 0$, then $div\ \underline{\tau} = 0$.

Proof of (ii). Consider the *identity* for *any* symmetric tensor $\underline{\underline{S}}$ and any vector $\underline{u}$:

$$div[\underline{\underline{S}} \cdot \underline{u}] = \underline{\underline{S}}:grad\ \underline{u} + \underline{u} \cdot div\ \underline{\underline{S}}$$

and the identification $\underline{\underline{S}} = \underline{\underline{T}}$, stress tensor, $\underline{u} = \underline{v}$ relative velocity field with respect to $\underline{X}$. Thus, we have:

$$div[\underline{\underline{T}} \cdot \underline{v}] = \underline{\underline{T}}:grad\ \underline{v} + \underline{v} \cdot div\ \underline{\underline{T}}$$

which is valid everywhere. Consider a region $\&_X$ enclosing $\underline{X}$. The relative velocity field is first order in x, so $v \to 0$ as $|x| \to 0$ and

$$div[\underline{\underline{T}} \cdot \underline{v}] = \underline{\underline{T}}:grad\ \underline{v} \text{ at } \underline{X}$$

provided that $div\ \underline{\underline{T}}$ is bounded. At point $\underline{X}$ viscous and pressure work are matched by viscous dissipation.

Region $\&_X$ is defined as:

$$\int_{\&_X}[div[\underline{\underline{T}} \cdot \underline{v}] - \underline{\underline{T}}:grad\ \underline{v}]dV = o(|\underline{x}|^4)$$

where $\underline{X}$ denotes the size of $\&_X$. For div $\underline{\underline{T}}$ bounded, we have:

$$\lim_{\&_X \to 0} \frac{\int_{\&_X}[div[\underline{\underline{T}} \cdot \underline{v}] - \underline{\underline{T}}:grad\ \underline{v}]dV}{\&_X} = 0$$

Note that for Newtonian incompressible fluids all that is required is $grad\ p$ be bounded in since $div\ \underline{\tau} = 0$ in the irrotational neighborhood of $\underline{X}$.

NOTATION

$A(t)$	= area of finite material surface
$A(z)$	= cross sectional area in continuous mixer
a_v	= intermaterial area per unit volume
$\hat{a}$	= normal (Frenet triad)
$\hat{b}$	= binormal (Frenet triad)
$d\underline{x}$	= differential vector
$d\underline{X}$	= differential vector in reference state
ds, dS	= differential element of surface
dv, dV	= differential element of volume
$\hat{d}_1$, $\hat{d}_2$, $\hat{d}_3$	= maximum directions of stretching
$\underline{\underline{C}}$	= Cauchy-Green strain tensor
$eff(z)$, $\overline{eff(t)}$	= mixing efficiencies
$\underline{\underline{F}}$	= deformation tensor
$f(\underline{x})$	= generic scalar function
$\underline{\underline{I}}$	= unit tensor
$K_{\mathscr{L}}$, $K_{\mathfrak{S}}$	= curvature of Line $\mathscr{L}$ and surface $\mathfrak{S}$
$\mathscr{L}$	= material line, $\mathscr{L}_t$ configuration at time t
$L(t)$	= length of finite material line
$\underline{\underline{L}}$	= velocity gradient
$\hat{M}$	= local tangent unit vector in material line $\mathscr{L}_0$
$\hat{m}$	= local tangent unit vector to material line $\mathscr{L}_t$
$\hat{N}$	= local normal unit vector in material surface $\mathfrak{S}_0$
$\hat{n}$	= local normal unit vector in material surface $\mathfrak{S}_t$
$\&_X$	= microflow element
s	= striation thickness
$\mathfrak{S}$	= material surface, $\mathfrak{S}_t$ configuration at time t
$\underline{\underline{T}}$	= stress tensor
t	= time, t' and t'' variables of integration
$\underline{v}$	= velocity vector
$\underline{x}$	= vector from point $\underline{X}$
$\underline{X}$	= Lagrangian coordinate, particle $\underline{X}$
z	= axial distance

Greek Letters

η	= area stretch
λ	= lineal stretch
μ	= viscosity
$\underline{\underline{\tau}}$	= viscous part of stress tensor
$\underline{\tau}$	= stress vector
$\underline{\chi}$	= motion $\underline{x} = \underline{\chi}(\underline{X}, t)$
$\underline{\underline{\Omega}}$	= vorticity tensor

Superscripts

T	= transposed of tensor
-1	= inverse of tensor
$*$	= reduced variable
—	= quantity in frame $\bar{F}$

Special Symbols

$=$	= volume average
⟨⟨ ⟩⟩	= mixed cup average
—	= area average
{ }	= set
∩	= intersection
< >	= mean value
∈	= belongs to

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