
Introduction

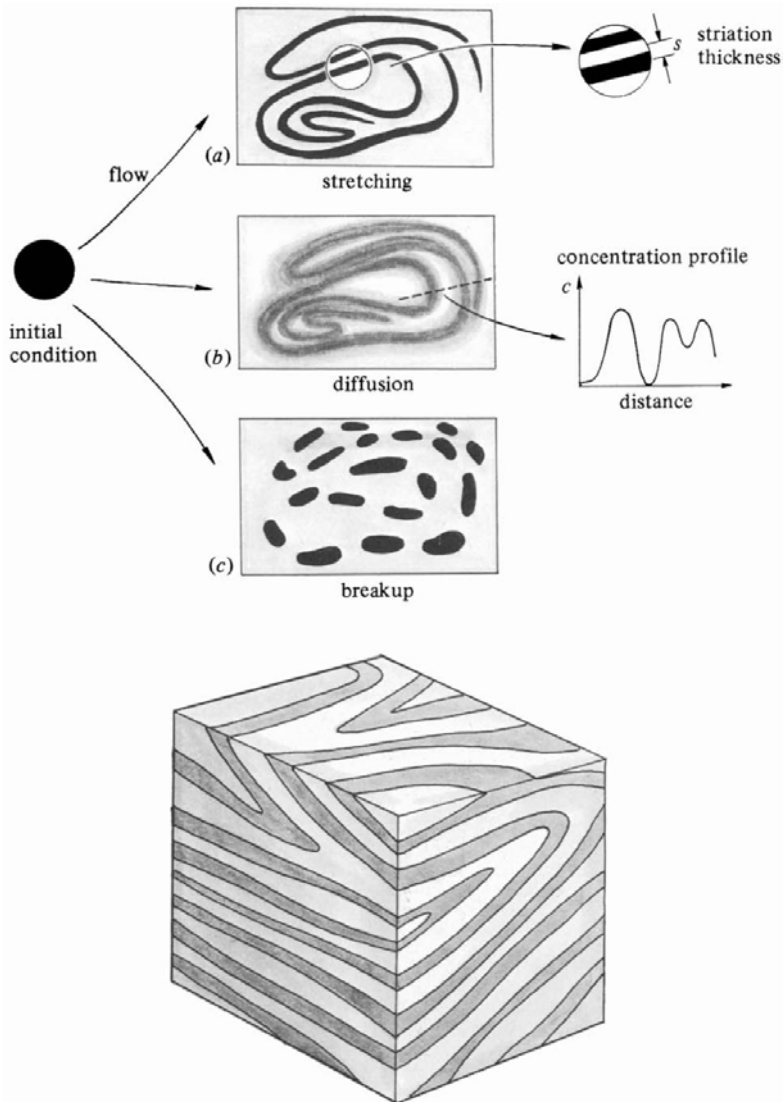
1.1. Physical picture

In spite of its universality, mixing does not enjoy the reputation of being a very scientific subject and, generally speaking, mixing problems in nature and technology are attacked on a case-by-case basis. From a theoretical viewpoint the entire problem appears to be complex and unwieldy and there is no idealized starting picture for analysis; from an applied viewpoint it is easy to get lost in the complexities of particular cases without ever seeing the structure of the entire subject.

Figure 1.1.1, which we will use repeatedly throughout this work, describes the most important physics occurring during mixing. In the simplest case, during mechanical mixing, an initially designated material region of fluid stretches and folds throughout the space. This is indeed the goal of visualization experiments where a region of fluid marked by a suitable tracer moves with the mean velocity of the fluid. This case is also closely approximated by the mixing of two fluids with similar properties and no interfacial tension (in this case the interfaces are termed passive, see Aref and Tryggvason (1984)).

Obviously, an exact description of the mixing is given by the location of the interfaces as a function of space and time. However, this level of description is rare because the velocity fields usually found in mixing processes are complex. Moreover, relatively simple velocity fields can produce very efficient area generation in such a way that the combined action of stretching and folding produces exponential area growth. Whereas this is a desirable goal in achieving efficient mixing it also implies that initial errors in the location of the interface are amplified exponentially fast and numerical tracing becomes hopeless. More significantly, this is also a signature of *chaotic* flows and it is important to study the conditions under which they are produced (more rigorous definitions of *chaos* are given in Chapters 5 and 6). However, without the action of molecular diffusion, an instantaneous cut of the fluids reveals a *lamellar structure* (Figure 1.1.1). A measure of the state of mechanical mixing is given by

Figure 1.1.1. Basic processes occurring during mixing of fluids: (a) corresponds to the case of two similar fluids with negligible interfacial tension and negligible interdiffusion; an initially designated material region stretches and folds by the action of a flow; (b) corresponds to a blob diffusing in the fluid; in this case the boundaries become diffuse and the extent of the mixing is given by level curves of concentration (a profile normal to the striations is shown at the right); in (c) the blob breaks due to interfacial tension forces, producing smaller fragments which might in turn stretch and break producing smaller fragments. Case (b) is an excellent approximation to (a) if diffusion is small during the time of the stretching and folding. In (a) the blob is *passive*, in (c) the blob is *active*.



the thicknesses of the layers, say s_A and s_B and $\frac{1}{2}(s_A + s_B)$ is called the *striation thickness* (see Ottino, Ranz, and Macosko, 1979). The amount of interfacial area per unit volume, interpreted as a structured continuum property, is called the *intermaterial area density*, a_v . Thus, if S designates the area within a volume V enclosing the point \mathbf{x} at time t ,

$$a_v(\mathbf{x}, t) = \lim_{V \rightarrow 0} \frac{S}{V}.$$

Some of the above concepts require modification if the fluids are miscible or immiscible. If the fluids are immiscible, at some point in the mixing process the striations or blobs do not remain connected and break into smaller fragments (Figure 1.1.1(c)). At these length scales the interfaces are not *passive* and instead of being convected (passively) by the flow, they modify the surrounding flow, making the analysis considerably more complicated (in this case the interfaces are termed *active*, see Aref and Tryggvason, 1984). If the fluids are miscible we can still track material volumes in terms of a (hypothetical) non-diffusive tracer which moves with the mean mass velocity of the fluid or any other suitable reference velocity. Designated surfaces of the tracer remain connected and diffusing species traverse them in both directions.¹ However, during the mixing process, connected iso-concentration surfaces might break and cuts might reveal islands rather than striations (Figure 1.1.1(b)). In this case the specification of the concentration fields of $n - 1$ species constitutes a complete description of mixing but it is also clear that this is an elusive goal.

Thus, it is apparent that the goal of mixing is reduction of length scales (thinning of material volumes and dispersion throughout space, possibly involving breakup), and in the case of miscible fluids, uniformity of concentration.² With this as a basis, we discuss a few of the ideas used to describe mixing and then move to examples before returning to the problem formulation in Section 1.4.

1.2. Scope and early works

A cursory examination of an eclectic and fairly arbitrary listing of some of the earliest references in the literature gives an idea of the scope of mixing processes and the ways in which mixing problems have been attacked in the past.³

G. I. Taylor (1934) The formation of emulsions in definable fields of flow, *Proc. Roy. Soc.*, **A146**, 501–23.

A. Brothman, G. N. Wollan, and S. M. Feldman (1945) New analysis provides formula to solve mixing problems, *Chem. Metal. Eng.*, **52**, 102–6.

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J. M. Ottino

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- W. R. Hawthorne, D. S. Wendell, and H. C. Hottel (1948) Mixing and combustion in turbulent gas jets, p. 266–88 in *Third Symp. on Combustion and Flame and Explosion Phenomena*, Baltimore: Williams & Wikens.
- C. Eckart (1948) An analysis of the stirring and mixing processes in incompressible fluids, *J. Marine Res.*, **VII**, 265–75.
- R. S. Spencer and R. M. Wiley (1951) The mixing of very viscous liquids, *J. Coll. Sci.*, **6**, 133–45.
- P. V. Danckwerts (1952) The definition and measurement of some characteristics of mixtures, *Appl. Sci. Res.*, **A3**, 279–96.
- P. V. Danckwerts (1953) Continuous flow systems-distribution of residence times, *Chem. Eng. Sci.*, **2**, 1–13.
- P. Welander (1955) Studies on the general development of motion in a two-dimensional, ideal fluid, *Tellus*, **7**, 141–56.
- S. Corrsin (1957) Simple theory of an idealized turbulent mixer, *A.I.Ch.E. J.*, **3**, 329–30.
- W. D. Mohr, R. L. Saxton, and C. H. Jepson (1957) Mixing in laminar flow systems, *Ind. Eng. Chem.*, **49**, 1855–57.
- Th. N. Zweitering (1959) The degree of mixing in continuous flow systems *Chem. Eng. Sci.*, **11**, 1–15.

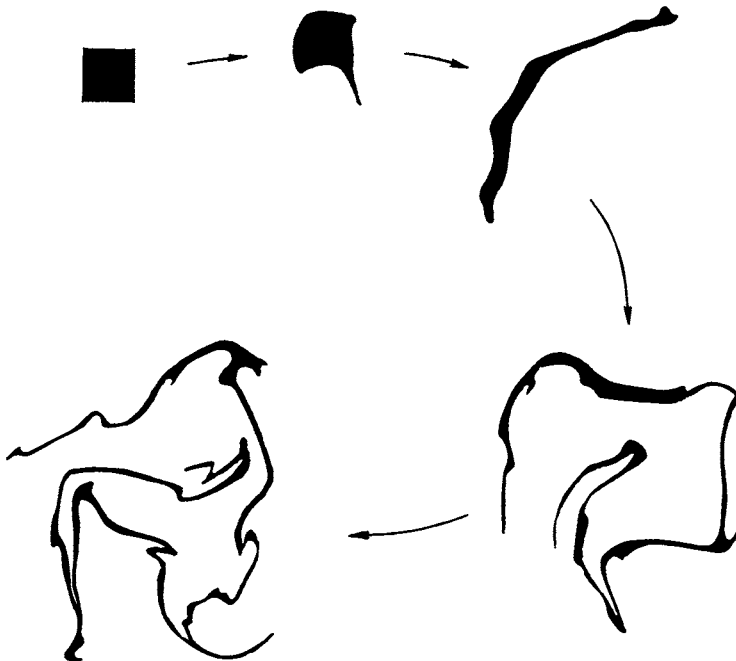
It seems at first strange to start a discussion on mixing with Taylor's 1934 paper. However, there are several reasons. The first one is that the problem is of practical importance and was attacked with the best tools of the time, both theoretically and experimentally. The second one is that the natural extension of his ideas to mixing remain largely unfulfilled. Taylor's concerns are obvious from the title of the paper. He distilled the essence of the problem, in general a complex one, and reduced the question to a *local* analysis: the deformation, stretching, and breakup of a droplet in two prototypical flows – planar hyperbolic flow and simple shear flow.⁴ Presumably, the long range goal was to mimic a complex velocity field in terms of populations of these two flows.⁵ This is similar, in spirit, to the approach adopted in this work, in two respects: (i) analysis of simple building blocks which give useful powerful insights into the behavior of complex problems, and (ii) decomposition of a problem in *local* and *global* components (this idea is reconsidered in Chapter 9).

Brothman, Wollan, and Feldman (1945) had more practical and pressing needs in mind and tried to attack the problem of mixing in a general and abstract way. They spoke of fluid deformation and [fluid] rearrangement, and regarded mixing as a three-dimensional shuffling process. They worked out probabilistic arguments directed predominantly to mixing in closed systems, such as stirred tanks, and obtained kinetic expressions for the creation of interfacial area. Eckart (1948) had in mind substantially larger length scales and started his analysis with the continuum field equations and calculated the 'mixing times' of thermal and

saline spots in oceans without resorting to any mechanistic description of the process. A conceptually similar problem in terms of scales, mixing in atmospheric flows, was addressed by Welander (1955). Remarkably, he did so by considering the possibility of applying Hamiltonian mechanics to ideal fluids and stressed the need for studying the stretching and folding of material elements in the flow and devised formulas to follow the process. The growth of a material line by fractal construction is also explained in his work as well as a treatment of motion of point vortices from a Hamiltonian viewpoint. He also performed experiments and one of his visualizations is reproduced in Figure 1.2.1.⁶

The interactions between turbulence and chemical reactions is of utmost importance in combustion. Although the approach to these problems in the 50's and 60's was largely statistical this was not always the case and it is comforting to know that in well thought out experimental papers such as the one by Hawthorne, Wendell, and Hottel (1948) one finds descriptions emphasizing the geometrical aspects of the problem. To quote

Figure 1.2.1. Reproduction of one of the early mixing experiments of Welander (1955); evolution of an initial condition in a rotating flow. He used butanol floated on water and the initial condition (square) was made of methyl-red; unfortunately few additional details regarding the experiment were given in the original paper.



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from their paper,

According to the physical picture of the turbulent flame, eddies . . . are being drawn in from the surrounding atmosphere and being broken up into particles of various sizes . . . The total area of flame envelope is many times the area available in a diffusion flame but nevertheless the final intimate mixing of the gas and oxygen must occur between eddies as a result of molecular diffusion.⁷

Subsequently, statistical theory took over and the geometrical aspects of the problem were somewhat lost. Of the many possible offsprings of the statistical theory of turbulence to mixing (e.g., Batchelor, 1953) we might mention the short but influential paper by Corrsin (1959) which proposed a simple model to calculate the rate of decrease of concentration fluctuations in an ideal, yet subsequently widely used mixer.⁸ Another important concept based on statistical reasoning is that of the mixing length theory (Prandtl, 1925; Schlichting, 1955, Chap. XIX), which has found application in an enormous range of problems ranging from chemical engineering (Bird, Stewart, and Lightfoot, 1960) to astrophysics (Chan and Sofia, 1987, Wallerstein, 1988). Even though the statistical treatment does not lend itself easily to visualization, notable exceptions exist and many of the early works focused on the stretching of material lines and surfaces, for example, Batchelor (1952; also Corrsin, 1972) analyzed the problem theoretically, whereas Corrsin and Karweit presented experimental results (Corrsin and Karweit, 1969). Other work focused on local deformation to capture the details of the turbulent motion at small scales. For example, Townsend (1951) performed an analysis of deformation and diffusion of small heat spots in order to interpret experimental Eulerian data in homogeneous decaying turbulence.

Concurrently, at the other end of the spectrum, the stretching of material lines and volumes was also a concern in the mixing of liquids in low Reynolds number flows. Spencer and Wiley (1951) focused on the mixing of very viscous liquids and stressed the idea of being able to describe the growth of interfacial area between two fluids and the need to relate the results to the fluid mechanics. However, even though the mathematical apparatus, largely developed in continuum mechanics, was already in place for such a program, it was not until much later that such developments took place and most of what followed from Spencer and Wiley's work was confined to deformation in shear flows. Two other points worth mentioning from their work, which have a clear relationship with dynamical systems, are the identification of stretching and cutting or folding as the primary mixing mechanism, the so-called 'baker's transformation' characteristic of chaotic systems (see Chapter 5), and the idea

of representing mixing processes in terms of matrix transformations, which is obviously related to mappings (see Chapter 5) and transition matrices (see p. 164 in Reichl, 1980). A closely related study by Mohr, Saxton, and Jepson (1957) also focused on viscous liquids in the context of polymer processing. They considered the stretching of a filament of a fluid in the bulk of another one in a shear flow using simple arguments to account for the viscosity of the fluids but without taking into account the interfacial tension. The problem is similar in spirit to the one treated by Taylor (1934) and much work could follow along these lines. Nevertheless this simplified treatment forms the basis for most of the subsequent developments in the mixing of viscous fluids.⁹

It is probably fair to say that most of the previous works have the geometrical interpretation given in Figure 1.1.1. However, a point of departure from this picture of significant consequence in chemical engineering took place with the papers by Zweitering (1959) and Danckwerts (1958). In this case the approach became more ‘lumped’ or macroscopic and the emphasis shifted to continuous flow systems and the characterization of mixing by the temporal distribution of exit times.¹⁰

Whereas the objective of most of the above works was to relate the fluid mechanics to the mixing or some knowledge of the process to the output, Danckwerts (1953) focused primarily on the characterization of the mixed state, i.e., he devised numbers or indices to indicate to the user how well mixed a system is (e.g., how well mixed is the system of Figure 1.3.1? Figure 1.3.3? Figure 1.3.4?). Even though we are going to say little about ‘the measurement of mixing’, this is probably the place to stress our opinion on a few points: (i) the measure should be selected according to the specific application and it is futile to devise a single measure to cover all contingencies, and (ii) the measurement has to be relatable to the fluid mechanics.

Examples

- (i) The striation thickness, s , Figure 1.1.1, is important in processes involving diffusing and reacting fluids and represents the distance that the molecules must diffuse in order to react with each other. In simple cases, s can be calculated exactly with a knowledge of the velocity field (see Chella and Ottino (1985a) and examples in Chapter 4).
- (ii) Molten polymers are often mixed (an operation often referred to as blending) to produce materials with unique properties. For example, in the manufacture of barrier polymer films it might be desirable to produce structures with low effective permeability. This requires that

the clusters of the more permeable materials are disconnected and do not form a percolating structure. However, the details of effective diffusion near the percolation point depend on the ramification of the clusters (Sevick, Monson, and Ottino, 1988). Even though such measurements can be extracted from electron micrographs (e.g., Figure 1.3.4, see color plates) via digital image analysis (Sax and Ottino, 1985), to date there are no models allowing the computation of such details from the fluid mechanics of the process.

- (iii) A model for the structure of the Earth's upper mantle (Allègre and Turcotte, 1986) postulates that the oceanic crust becomes entrained in the convective mantle where it is subsequently stretched into filaments by buoyancy induced motions. It follows that, on the average, the 'oldest' layers are the thinnest and that the diffusion processes concurrent with the stretching become important over geological time scales when the striation thickness is of the order of 0.1–1 m (the typical diffusion coefficients are of the order 10^{-14} – 10^{-16} cm²/s, which implies diffusion on time scales of the order of 10^{16} – 10^{20} s. By comparison the time scale based on the age of the Earth is 1.4×10^{17} s). In this case a model describing the entrainment of material in the convective mantle coupled to a model describing the evolution of the striation thickness as function of time is capable of describing the gross characteristics of the process.
- (iv) Consider Eulerian concentration measurements in a turbulent mixing layer. In principle, the fluctuations can be taken as an indication of the mixing between the streams and an index such as Danckwerts's intensity of segregation² can be computed. In the ideal case of a non-invasive probe with an infinitely fast response and vanishingly small resolution volume we obtain an indication of the thickness of the striations passing by the point as a function of time. However, even if this were possible, the statistics of the fluctuations would be very complicated and hard to connect to the fluid mechanics of the process itself. What is worse, however, is the inability of the measurements to give a correct global picture of large scale structures, the so-called coherent structures (Roshko, 1976). In this case a flow visualization study based, for example, on shadowgraphs is infinitely more revealing with regard to the structure of the flow (Brown and Roshko, 1974) (see also Figure 1.3.5; see color plates).

1.3. Applications and geometrical structure

It is clear that even restricting our attention to fluid–fluid systems,¹¹ miscible or immiscible, diffusive or non-diffusive, reacting or not, the scope of mixing problems is enormous and it is not possible to develop a complete and useful theory encompassing all the above situations. It is nevertheless evident that, in spite of the enormous range of length and time scales, the underlying geometrical structure associated with the process of reduction of length scales is that of Figure 1.1.1. In this section we highlight this aspect by means of a few examples.

Mixing is relevant in processes ranging from geological length scales (10^6 m) and exceedingly low Reynolds numbers (10^{-20}), such as in the mixing processes occurring in the Earth's mantle, to Reynolds number of order 10^{11} corresponding to mixing in oceans and the atmosphere.¹² An example of a simulation of mixing in the Earth's mantle is shown in Figure 1.3.1, in which the flow is modelled as a two-dimensional layer heated from below.¹³ In these cases, actual mixing experiments are of course impossible. However, laboratory models of large scale circulation in oceans can be carried out with liquids in containers placed on a rotating turntable sometimes involving combinations of sources and sinks. Figure 1.2.1, from the early paper by Welander (1955), shows an example (it is worth noting that the output of similar experiments, were described as 'chaotic', e.g., Veronis, 1973).

Undoubtedly, *chaotic* is an apt description of stretching in truly turbulent flows. Figure 1.3.2 shows the stretching of material lines in a turbulent, nearly isotropic, flow (Corrsin and Karweit, 1969), where the expectation¹⁴ is that of exponential growth (Batchelor, 1952). Note, however, the inherent limitation of experimental techniques in resolving the smallest scales.

The deformation of material lines has been studied also in the case of chaotic Stokes's flows. Experiments focusing on deformation of material lines were carried out by Chaiken *et al.* (1986) and Chien, Rising, and Ottino (1986). In the case of Chaiken *et al.* the flow consists in an eccentric journal bearing time-periodic two-dimensional flow which is described in detail in Chapter 7. Figure 1.3.3 shows the shape adopted by a material line of a tracer by the periodic discontinuous operation of the inner and outer cylinders in a counter-rotating sense. Note the absence of 'corners' and 'branches' in the folded structure even though the flow is essentially discontinuous (compare with Figure 1.2.1).

Figures 1.2.1 and 1.3.3 show complex stretched and folded structures, characteristic of mixing in two-dimensional flows. In both cases the

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structure formed is lamellar and an indication of the state of mixing is provided by the striation thickness. However, in other cases the structures obtained are considerable more complex. If the fluids are immiscible and sufficiently different, interfacial tension plays a dominant role at small

Figure 1.3.1. Deformation of a tracer in a numerical experiment of motion in the Earth mantle. The sides of the rectangle are insulating but the bottom is subjected to a constant heat flux while the temperature of the top surface is kept constant. The motion is produced by buoyancy and internal heating effects (the fluid is heated half from below and half from within). The Rayleigh number is 1.4×10^6 , the time scale of the numerical simulation corresponds to 155 Myear, and the thickness of the layer is 700 km. An instantaneous picture of the streamlines reveals five cells. (Reproduced with permission from Hoffman and McKenzie (1985).)

