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Mixing: physical issues

This chapter provides a brief review of physical considerations in the analysis of mixing problems and several examples of problems that can be framed in terms of the mathematical structure covered in this book.

Mixing is a common phenomenon in everyday life. A blob of white cream placed in a cup of black coffee and gently stirred with a spoon forms, if one looks carefully, intricately shaped striated structures, until the mixture of coffee and cream homogenizes into a fluid that is uniformly brown in colour. This common phenomenon serves to illustrate some of the key features of mixing; namely, the interplay between advection and diffusion. If the coffee is at rest when the cream is added (and assuming that the insertion of the cream into the coffee only causes negligible disturbance of the surrounding coffee) then, in the absence of stirring, the cream mixes with the coffee by the mechanism of molecular diffusion. Experience tells us that in this particular situation the mixing takes much longer than we would typically be willing to wait. Therefore we stir the admixture of coffee and cream with a spoon, and observe it to homogenize very quickly. This stirring illustrates the role that advection plays in homogenizing the cream and coffee. In fact, in this particular example (as well as many others) the role of molecular diffusion in achieving the desired final mixed state may very well be negligible.

In this monograph we will concentrate exclusively on mixing via convective motions or advection. This is the foundation upon which the entire subject of mixing is built. Of course, the impact or lack thereof of molecular diffusion on mixing is a fact that requires justification, and this justification occurs within the physical context of specific mixing problems. The spectrum of problems occurring in nature and technology where mixing is important is enormously wide (see Figure 1.1). For example, in the subject of mantle convection (Kellogg (1993)) it probably seems reasonable that diffusion has essentially no impact on the mixing of 'rock with rock'. At the other end of the spectrum, in the realm of the very small, mixing in microfluidic devices is another area in which diffusion may have a negligible effect. In this setting the goals are to mix quickly and in

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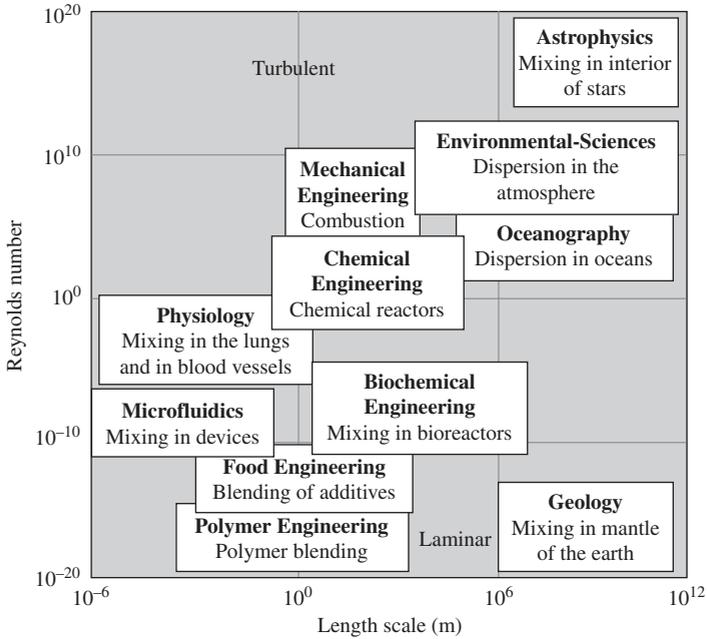
Figure 1.1 Spectrum of mixing problems. [Adapted from Ottino (1990).]

small spaces, and achieving these goals tends to make the effects of diffusion negligible and to prohibit the creation of turbulent flows, which are well known to enhance mixing. In fact the subject of mixing at the microscale is tailor made for the mathematical approach of 'chaotic mixing' and the dynamical systems approach, about which now there is a very large literature (see, for example Ottino (1989a, 1990), Wiggins (1992), Wiggins & Ottino (2004)).

The dynamical systems approach to mixing, in the absence of diffusion, is the central theme of this book. But more precisely, we develop the notion of the *linked twist map* (LTM) as a paradigm for chaotic mixing in that it embodies the kinematic mechanism of 'streamline crossing' as a mechanism for generating chaotic fluid particle trajectories. But most importantly, the LTM framework provides a way in which mixing can be optimized in the sense that one can give conditions under which mathematically rigorous characterizations of strong mixing occur on regions of nonzero area. Of course, the conditions leading to strong mixing in regions of nonzero area do not guarantee fast mixing, something one wishes to produce in practice. However, not satisfying the conditions guarantees that mixing will not be widespread, an outcome which is clearly undesirable. Thus, in a strict sense, the conditions described in this book are necessary conditions for effective mixing.

Before developing this approach in some detail, and describing how LTMs naturally arise in the context of a variety of mixing problems, we first consider some general physical and kinematic considerations of mixing in general that will provide rough, but essential, guides to understanding the issues relating to 'good' and 'bad' mixing.

1.1 Length and time scales

In any 'mixing problem' a consideration of length and time scales is fundamental as they provide an indication of the main mechanisms at work. Dimensional quantities, such as length and time scales, often combine with certain material parameters (e.g., molecular diffusivity, viscosity, etc.) to form dimensionless ratios that provide rough guides to the relative importance of competing mechanisms. The Reynolds number, Re, is the ratio of inertial forces to viscous forces. If U and L denote characteristic velocity and length scales, Re is UL/ν, where ν is the kinematical viscosity, which is the ratio of viscosity, μ, and density, ρ, i.e, $\nu = \mu/\rho$. Small values of Re correspond to viscous dominated (or laminar) flows, and large values of the Reynolds number correspond to turbulent flows (see examples in Figure 1.1). The Péclet number, Pe, is the ratio of transport by advection (or convection) and by molecular diffusion; Pe is defined as $\mathsf{Pe} = UL/D$, where D is the molecular diffusion coefficient. Pe can be interpreted also as the ratio of diffusional to advective time-scales; the time scale for diffusion is L^2/D and the time scale for convection is L/U. A large value of Pe indicates that advection dominates diffusion, and a small Pe indicates that diffusion dominates advection, or, in terms of time-scales, the fastest process dominates. The ratio Re/Pe is ν/D, the ratio between two transport coefficients, the so-called Schmidt number, $Sc = \nu/D$. Sc can be interpreted as the ratio of two speeds. The speed of propagation of concentration is $\delta_D \sim (Dt)^{1/2}$, the speed at which concentration gets smoothed out, whereas the propagation of momentum is $\delta_V \sim (\nu t)^{1/2}$, the speed that it takes for motion to spread out or die. The ratio of these two speeds, $(\mathrm{d}\delta_V/\mathrm{d}t)/(\mathrm{d}\delta_D/\mathrm{d}t)$ is $Sc^{1/2}$; thus if $Sc \gg 1$, as in the case of liquids, concentration fluctuations survive without being erased by mechanical mixing until late in the process. We will encounter these and other numbers in the following examples. As a reference point the kinematic viscosity of water is about $0.01\,\mathrm{cm}^2/\mathrm{s}$ and of air $0.15\,\mathrm{cm}^2/\mathrm{s}$; somewhat surprisingly momentum spreads more quickly in air than in water. The value of ν in liquids is highly dependent on temperature. The diffusion coefficient of small molecules in water is about $10^{-5}\,\mathrm{cm}^2/\mathrm{s}$; thus a

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typical value of *Sc* for a liquid such as water is about 10^3. For gases *Sc* is of order one.

Example: mixing in a coffee cup

Consider again the case of mixing of milk in a coffee cup. Assume that the cup's characteristic length is $L \sim 4$ cm and that the typical speed is $U \sim 5$ cm/s. Then the Reynolds number is approximately 2,000, indicating that advection is much more important than viscous effects; a few strategic turns of the spoon get the job done. Even if the spoon is held in place the wake behind the spoon mixes the fluid (the wake flow behind a stationary object being a well-studied problem). Mixing of milk in golden syrup is another matter. The kinematical viscosity of golden syrup at 15°C is $1200 \, \text{cm}^2/\text{s}$, so $\mathsf{Re} \sim 10^{-2}$. In this case viscous effects dominate and one cannot rely on inertia; the spoon is removed and the motion stops. An estimate of the time it takes for the motion to die off is L^2/ν. In the case of syrup the motion stops in a hundredth of a second whereas in the case of milk the estimate is half an hour. Advection dominates molecular diffusion in both problems, $\mathsf{Pe} \sim 10^6$ in the case of milk and syrup. The time necessary for mixing relying solely on molecular diffusion is L^2/D. The estimate in this case is in the order of more than a day for either problem.

Example: flow in a small channel

Consider the flow of two adjacent streams of fluid in a channel of length L along the z-direction having a cross-sectional area in the plane xy with a characteristic length h describing the width of the channel in the cross-section. The velocity in the z-direction is denoted $v_z(x, y)$ with a mean value U. In microfluidic applications typical numbers are $h \sim 200 \, \mu\text{m}$, and $\mu/\rho \sim 10^{-2} \, \text{cm}^2/\text{s}$. Take U as 1 cm/s. The Reynolds number in this case is $\mathsf{Re} = Uh/\nu \sim 2$. This small value of the Reynolds number implies that flows in microfluidic channels are typically viscous dominated. The no-slip boundary condition on the walls of the channel leads to velocity profiles having parabolic shapes (i.e. at a given cross-section, $v_z(x, y)$ is zero on the walls, and increases monotonically to a maximum near the middle of the channel). Consider now the Péclet number. A typical molecular diffusion coefficient ranges between $10^{-5} \, \text{cm}^2/\text{s}$ at the high end (corresponding to a small molecule) and $10^{-7} \, \text{cm}^2/\text{s}$ at the low end (typical of large molecules; e.g. haemoglobin in water corresponds to $10^{-7} \, \text{cm}^2/\text{s}$). Thus, the typical values of advective to diffusional time scales range between 10^3 and 10^5 indicating that advection is much faster than molecular diffusion. Thus, in spite of the small dimensions, molecular diffusion may

not be counted on to homogenize the system to molecular scales in a reasonable amount of time. This can be seen also by calculating time required for diffusion, t_D (i.e., neglecting advection) to move a particle the width of the channel, $t_D \sim h^2/D$. This is 40 seconds for $D \sim 10^{-5} \, \mathrm{cm}^2/\mathrm{s}$, to about one hour for $D \sim 10^{-7} \, \mathrm{cm}^2/\mathrm{s}$.

Example: more on channel flow

Suppose that the two entering fluid streams flowing side by side in the channel are miscible. Then molecular diffusion provides a mechanism for the streams to penetrate into each other. The distance of penetration of one stream into another due to diffusion, δ_D, at time t, is $\delta_D \sim (Dt)^{1/2}$. Both fluids occupy the entire width of the channel after they have flowed a distance Ut_D down the channel. This distance ranges from 40 cm to 4000 cm depending on the value of D. These distances may be prohibitively long for typical microfluidic applications.

These estimates lead to three related observations important in channel flows:

- First, let us revisit the notion of 'penetration distance' discussed above from an alternate point of view. As we have seen, to reach $\delta_x = h$ solely relying on molecular diffusion takes a time $\sim h^2/D$. So if the streams move with speed U this process will have occurred after the streams have flowed a distance $L \sim U(h^2/D)$ along the channel (i.e., in the z direction). From the definition of Péclet number given above, this gives $L/h \sim \mathsf{Pe}$. Given the typical (large) values of Pe, this may be unacceptably high for microfluidic applications.

- The second observation is that as diffusion takes place in the cross-section of the channel (the plane x–y), particles experience a range of velocities (recall that the flow is parabolic), resulting in concentration dispersion in the z-direction and in a dispersion coefficient (Taylor dispersion) that scales as $1/D$. This means that fluid that disperses slowly in the cross-section will disperse rapidly in the z-direction, and vice versa.

- The third and final observation is also a consequence of the parabolic nature of the velocity field. The residence time distribution is a standard diagnostic for quantifying mixing in channel flows. Roughly, it is a probability density function consisting of the number of particles that reach the end of the channel in a given time. Near the wall the velocity field is linear with distance, $v_z \sim \dot{\gamma} d$, and thus a particle a distance d away from the wall takes a time $L/(\dot{\gamma} d)$ to reach L (hence $\dot{\gamma}$ is the shear rate at the wall). Therefore particles near the wall (as $d \to 0$) take a long time to reach the end of the channel. This would result in 'long tails' in the residence time

distribution (RTD) for particles in the channel. Moreover the fluid near the wall never co-mingles with fluid elements in the centre of the channel. The result is that mixing is poor.

Putting all this together, it is then clear that the key to effective mixing in a channel lies in the ability to mix material in the *cross-section* – to create a large amount of contact interface between the two fluids. Material 'sticking' to walls is bad for mixing. Two advantages come with enhanced mixing in the cross-section. The first is that if particles explore all of the cross-section (i.e., *x–y* space) in a random manner they will experience all velocities (slow near the walls, fast near the centreline) and on the whole the broadening of the RTD is reduced. The second advantage has to do with transfer processes between the surface of the device and the bulk of the fluid. If mixing is effective diffusional processes are greatly accelerated; material that is near the wall goes into the bulk and vice versa, thereby eliminating a slowdown due to diminishing concentration gradients.

1.2 Stretching and folding, chaotic mixing

In the previous section there was essentially no explicit discussion of geometric aspects of the mixing of two fluids. Geometrical considerations are motivated by the fact that the objective of mixing is to produce the maximum amount of interfacial area between two initially segregated fluids in the minimum amount of time or using the least amount of energy. Creation of interfacial area is connected to stretching of lines in 2D and surface in 3D. A fluid element of length $\delta(0)$ at time zero has length $\delta(t)$ at time t; the *length stretch* is defined as $\lambda = \delta(t)/\delta(0)$; if mixing is effective λ increases nearly everywhere, though there can be regions of compression where $\lambda < 1$. In simple shear flow the fastest rate of stretching, $d\lambda/dt$, corresponds to when the element passes though the 45° orientation corresponding to the maximum direction of stretching in shear flow; for long times the stretching is linear in time, $\lambda \sim t$, as the element becomes aligned with the streamlines. In an elongational flow (e.g., a flow where the velocity field depends linearly on the spatial variables and contains a saddle type stagnation point) the rate of stretching is exponential, $\lambda \sim e^t$. The distance between striations is inversely proportional to the surface area and the thinner the striations the faster the diffusion. Note that the effects of stretching on accelerating diffusion enter in two different ways: more interfacial area means more area for transfer; at the same time diminishing striation thicknesses increases the concentration gradients and increases the mass flux.

In order to conceptualize the growth of interfacial area (or perimeter in the case of two dimensions), we can imagine small elements, area or line. If mixing is effective, the small elements grow in area or length (ideally, this happens everywhere in the flow; in practice some elements may get compressed). As we shall see, the striation thickness, and stretching, are related in a deep way to dynamical systems concepts – entropy, finite size Lyapunov exponents, Smale horseshoe maps (discussed in Chapter 4), and the Baker's transformation (discussed in Chapter 3).

The key to effective mixing lies in producing stretching and folding; stretching and folding may be roughly equated with chaos as we will see in later chapters. The simplest case corresponds to two dimensions. If the velocity field is steady, the mixing is poor, stretching for long times is linear, as in the case of a simple shear flow; i.e., the stretching *rate* of line elements or decays as $1/t$ (we are restricting ourselves to bounded flows; that is, we are excluding unbounded elongational flows). It is, however, relatively straightforward to produce flow fields that can generate stretching and folding and hence chaos.

Experience over the past twenty years shows that a sufficient (heuristic) condition for chaos is the 'crossing' of streamlines. That is, two successive streamline portraits, say at t and $t + \Delta t$ for time periodic two-dimensional flows, or at z and $z + \Delta z$ for spatially periodic flows, when superimposed, should show intersecting streamlines when projected onto the *x*–*y* plane. In two-dimensional systems this can be achieved by time modulation of the flow field, for example by motions of boundaries or time periodic changes in geometry. In this monograph we show that this criterion is encapsulated by *linked twist maps* (LTMs). Figure 1.2 from Ottino & Wiggins (2004) shows a schematic representation of a channel type micromixer constructed from the concatenation of basic mixing elements. In this illustration we consider the minimal number of different mixing elements, two. Cross-sectional streamline patterns at the end of each mixing element are shown. The details of the shape and internal structure of the channel are purposefully not shown. The point here is that they can be anything that produces the desired cross-sectional flow. We illustrate the mixing properties by placing red and blue 'blobs' at the beginning of the mixer and observing how they mix as they travel down the length of the mixer. This mixer can be analyzed with the LTM formalism, which provides sufficient conditions for (mathematically) optimal mixing. It is significant to note that a (seemingly) slight change in the streamline patterns can lead to a dramatic change in the mixing properties.

Numerous experimental studies have revealed the structure of chaotic flows. The most studied cases correspond to time-periodic flows. Dye structures of passive tracers placed in time-periodic chaotic flows evolve in an iterative
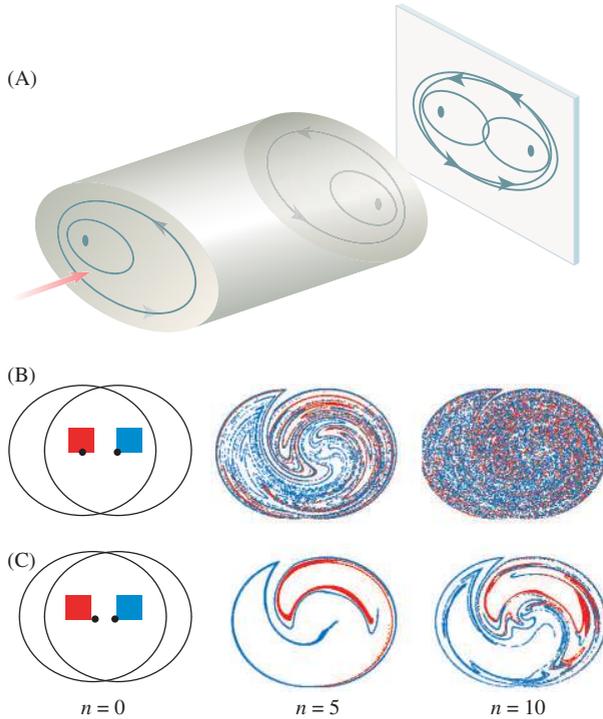
Figure 1.2 (A) Schematic representation of a channel type micromixer constructed from the concatenation of basic mixing elements. (B) The LTM mechanism causes the flow to mix completely after passing through five periodic elements of the mixer (where each consists of two of the basic mixing elements). (C) The LTM conditions are not satisfied and the flow exhibits islands, which result in poor, and incomplete mixing. [Figure taken from Ottino & Wiggins (2004).]

fashion; an entire structure is mapped into a new structure with persistent large-scale features, but finer and finer scale features are revealed at each period of the flow. After a few periods, strategically placed blobs of passive tracer reveal patterns that serve as templates for subsequent stretching and folding. Repeated action by the flow generates a lamellar structure consisting of stretched and folded striations, with thicknesses $s(t)$, characterized by a probability density function, $f(s, t)$, whose mean, on the average, decreases with time. The striated pattern quickly develops into a time-evolving complex morphology of poorly mixed regions of fluid (islands) and of well-mixed or chaotic regions. Islands translate, stretch, and contract periodically and undergo a net rotation, preserving their identity returning to their original locations. Stretching within islands, on average, grows linearly and much slower than in chaotic regions, in
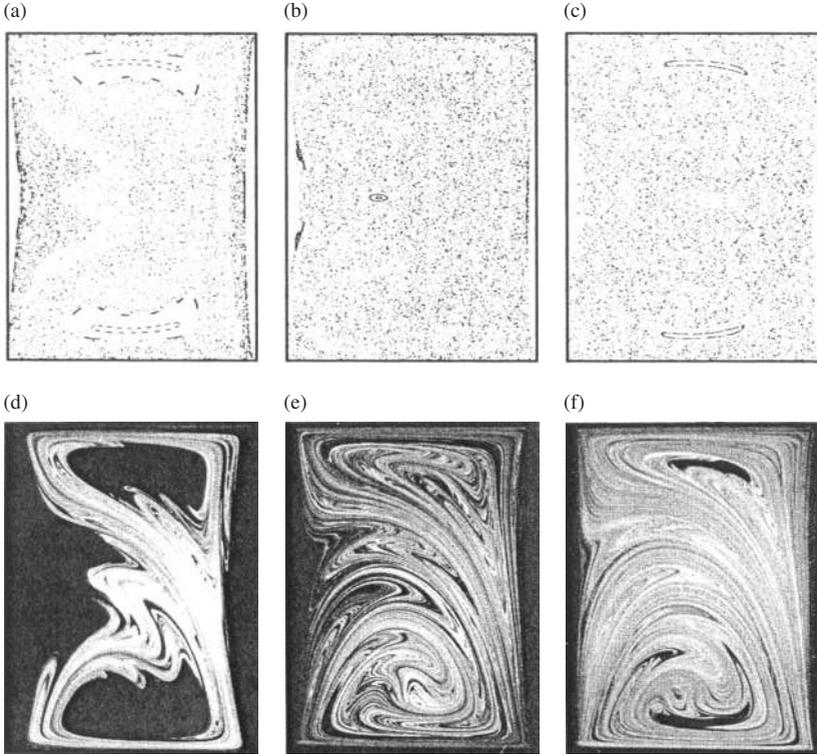
Figure 1.3 Panels (a)–(c) correspond to Poincaré sections of the cavity flow with three different protocols for the motion of the top and bottom boundaries. Immediately below each Poincaré section is a dye advection pattern for the same protocol. [Figure taken from Jana *et al.* (1994b).]

which the stretching increases exponentially with time. Moreover, since islands do not exchange matter with the rest of the fluid (in the absence of diffusion) they represent an obstacle to efficient mixing. Figure 1.3 from Jana *et al.* (1994b) shows Poincaré sections and dye advection patterns in a cavity. The flow is driven by moving the top and bottom boundaries according to a defined *protocol*. Three different protocols are shown, and each results in a different mixing pattern. By comparing the Poincaré sections to the dye advection patterns one easily sees that islands lead to poor mixing and chaos corresponds to 'good' mixing.

Now we consider a few aspects of mixing in a channel-like device: a duct flow. Duct flows are a basic configuration for many mixing devices. However, like steady two-dimensional flows, they are poor mixers. More precisely, duct

flows are defined by the following velocity field

$$v_x = \frac{\partial \psi}{\partial y}, \qquad v_y = -\frac{\partial \psi}{\partial x}, \qquad v_z = f(x, y).$$

That is, a duct flow is a two-dimensional cross-sectional flow augmented by a unidirectional axial flow. Note that in a duct flow, the cross-sectional and axial flows are independent of both time and distance along the duct axis.

Duct flows can be converted into efficient mixing flows (i.e., flows with an exponential stretch of material lines with time) by time-modulation or by spatial changes along the duct axis. One example of the spatially periodic class, is the classical partitioned pipe mixer (PPM). This flow consists of a pipe partitioned with a sequence of n orthogonally placed rectangular plates. The cross-sectional motion is induced through rotation of the pipe with respect to the assembly of plates whereas the axial flow is caused by a pressure gradient. There is one control parameter in the system: ratio of cross-sectional twist to mean axial flow, β (Khakhar *et al.* (1987), Kusch & Ottino (1992)). The flow is regular for no cross-sectional twist ($\beta = 0$), and becomes chaotic with increasing values of β. In Figure 1.4 we show Poincaré sections from Khakhar *et al.* (1987) for different values of β. The Poincaré sections are obtained by mapping particles under the flow from the cross-section of the flow at the beginning of one mixing element to the beginning of the next (see also Section 2.6). Notice how dramatically the distribution and sizes of islands and chaotic regions can change with β.

To give a few typical numbers, consider a striation thickness reduction, or equivalently length stretch, where the initial length scales $s(0) \sim h$ is reduced to a size $s(t_F)$ in an amount of time t_F. According to the typical numbers given earlier we take the typical shear rates in our device to be $\dot{\gamma} = U/(h/2) \sim 10^2 \, \text{s}^{-1}$. Consider a typical striation thickness reduction $s(0)/s(t_F)$ or length stretch $\lambda \sim 10^4$; that is a reduction from $10^2 \, \mu\text{m}$ to $10^{-2} \, \mu\text{m}$ or $10 \, \text{nm}$. At $10 \, \text{nm}$ molecular diffusion is fast at these scales, $10^{-7} \, \text{s}$ for $D = 10^{-5} \, \text{cm}^2/\text{s}$, to $10^{-5} \, \text{s}$ for $D = 10^{-7} \, \text{cm}^2/\text{s}$.

How long does it take to accomplish this striation thickness reduction? In simple shear, we have that $s(0)/s(t_F) \sim \dot{\gamma} t_F$; therefore the time needed to accomplish this reduction is $10^4/10^2 \, \text{s}^{-1} = 10^2 \, \text{s}$. An elongational flow on the other hand can accomplish the same reduction with a much lower value of elongational rate as compared with $\dot{\gamma}$; in this case $s(0)/s(t_F) = e^{\alpha t_F}$. Thus $\alpha = \ln(10^4)/100 \, \text{s} \sim 4 \times 10^{-2} \, \text{s}^{-1}$. Elongational flows are not practical; however a succession of simple shear flows with a periodic reorientation of the line elements accomplishes the same objective.