ago (Australia) and even 4 million years ago (Hawaii)—the sorts of time scales studied by Quaternary paleoecologists. They take advantage of a technique called "space-for-time" substitution, which allows them to study modern vegetation and soils on surfaces of different but known ages, and hence to infer what changes in ecology and soils took place over time. The application of space-for-time substitution to the study of ecosystem dynamics requires that assumptions be made, for example, that external factors remain constant and there are no major disturbances (*10*, *11*). Assumptions aside, the six chronosequences selected by Wardle *et al*. represent a unique "natural experiment" for determining consistent ecological features in the retrogressive phase of vegetational succession in temperate, tropical, and boreal vegetation.

These investigators report a unimodal response of tree basal area (a surrogate measure of tree biomass) over time. The tree basal area declines within 1000 to 10,000 years after the onset of primary succession. There is also an increase in the nitrogen to phosphorus (N:P) and carbon to phosphorus (C:P) ratios in humus in all six chronosequences, accompanied by a marked increase in the N:P ratio of litter in four of the chronosequences. These results imply that during retrogressive succession, P becomes limiting relative to N in the humus layer, followed by reduced P concentrations in the litter produced by vegetation in four of the chronosequences. Thus, unlike N, which is biologically renewable, P is not and is leached from soils over time, leading to a phosphorus-depeleted ecosystem.

As the authors demonstrate, declining tree biomass is often accompanied by reductions in litter decomposition rates and release of P from litter, as well as decreased activity of microbial decomposers. The proportion of fungi relative to bacteria increases as retrogressive succession proceeds. Fungal-based soil food webs retain nutrients better than do bacterial-based food webs, which suggests that during forest decline, nutrient cycling becomes more closed and nutrients become less available. The overall picture provided by Wardle *et al.* is that (in the absence of a major disturbance) there is a long-term decline in biomass accompanied by increasing P limitation relative to N, reduced rates of P release in decomposing litter, and reductions in litter decomposition, soil respiration, microbial biomass, and the ratio of bacterial to fungal biomass.

These findings, and the ecological processes proposed to explain them, provide an elegant model for the onset of the oligocratic phase of an interglacial, namely that tree biomass declines as P becomes increasingly limiting. Reductions in litter decomposition rates and changes in soil microbial assemblages may also occur. Paleoecologists have suggested that such changes may explain the long-term switch from forest soils composed of mull humus to those composed of mor humus (*2*, *8*, *9*). Given recent developments in paleoecology, paleolimnology, and stable-isotope analysis (*12–14*), paleoecologists now have tools to test directly some of the ideas proposed by Wardle and co-workers.

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APPLIED PHYSICS

# Designing Optimal Micromixers

**Julio M. Ottino and Stephen Wiggins**

Microfluidics is now part of big science and big business. It is a key component of established and developing technologies ranging from lab-on-a-chip biotech devices to inkjet printing. And the field is now bubbling with activity—thousands of papers are published and hundreds of patents are issued each year (*1*, *2*). A recent collection of papers (*3*) focuses on one aspect that is common to many of these technologies: mixing. Mixing—or lack thereof—is often a key obstacle to the effective functioning of microfluidic devices in many applications, and new ideas and approaches seem poised to have a major impact on the field.

Right now, the design of micromixers is largely a trial-and-error process, and new designs are driven by complex fabrication and fluid control techniques (such as microstereolithography and electro-osmosis). This situation may result in inefficiencies and suboptimal designs.

Mixing issues are complicated, and sometimes counterintuitive, because viscous effects dominate at small scales and viscosity-dominated flows are deterministic. Inducing turbulence—making the fluid motion random to improve mixing—is typically impractical. Molecular diffusion may help, but small spatial scales and short time requirements may render it ineffective. The only option at microfluidic scales is to have some knowledge of where the fluid particles go. As a result, our point of view must change from randomization to determinism, while still trying to "mix things up." Dynamical systems theory provides a suitable paradigm for deterministic mixing—chaos. Chaotic advection and chaotic mixing are typically far removed from the thinking of those who develop and use microfluidics. Nonetheless, some recent new ideas in microfluidic mixing have used chaos in a crucial manner (*3*). One very useful concept, for example, is generating helical motions in channels via surface patterning—a wall with small grooves oriented at oblique angles with respect to the axis of the main flow (*4*). This immediately suggests several possibilities for channel design involving combinations of corotating and counterrotating flows. But what combinations work best? Another concept is the disruption of a primary flow channel by cross-stream secondary flows (*5*). The questions here concern how to design the cross flows: how many are needed, how far apart should they be located, and so forth. One could also use droplets as mixers (*6*): When a drop moves though a straight channel, the flow within the droplet is axisymmetric; when the channel is curved, the symmetry is broken and the mixing within the droplet becomes chaotic. The questions here concern how to design the sequence of actions of axisymmetric flows, for how long they should act, and so on.

Mixer design starts from a central concept and evolves toward specificity by a se-

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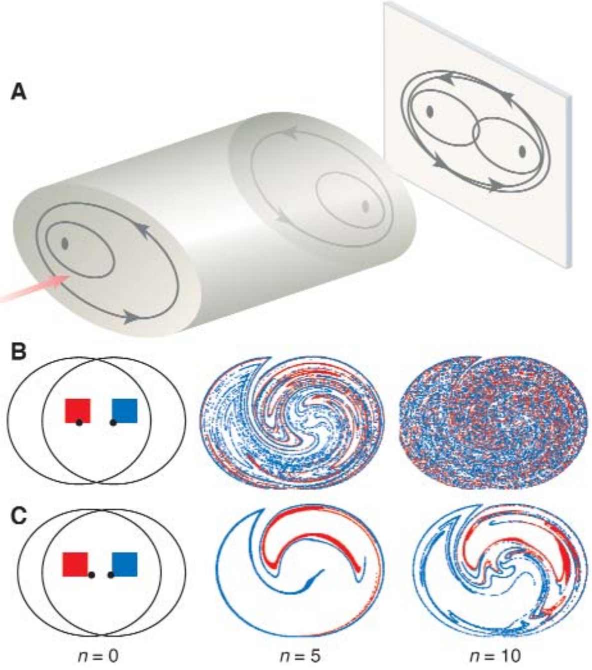
J. M. Ottino is in the Departments of Chemical and Biological Engineering and Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA. E-mail: jm-ottino@northwestern.edu S. Wiggins is in the School of Mathematics, University of Bristol, Bristol BS8 1TH, UK. E-mail: s.wiggins@bristol.ac.uk

ries of steps involving technological compromises and multiple decisions. The final systems, once a design is agreed upon, can be analyzed with computational fluid dynamics codes and the influence of the many parameters can be explored. However, this may be costly and inefficient, and may provide limited insight to researchers. The results of each computation are as specific as the results of a single experiment.

A unifying aspect of the three examples mentioned is that each suggests a family of designs. Optimizing global aspects of the family—playing with the big picture before descending into details—may result in a better design.

This is where a powerful idea, the so-called linked twist map (LTM), becomes useful (*7–11*). The literature on LTMs emerges from pure mathematics; indeed, LTMs were developed with no practical pursuits in mind. A twist map gives the motion of points, either after a fixed time or between two spatial locations, for a system with "circulating trajectories." An LTM is obtained when the dynamical system has a structure such that the motion can be described by the repeated application of two twist maps. They are abstractions of a type of Poincaré map used in celestial mechanics studies in the 1970s. However, LTMs immediately captured the attention of people in dynamical systems theory because, as a result of their geometrical structure, it was possible to rigorously prove "strong mixing properties" for them. Mathematicians in the area of ergodic theory have had a hierarchical classification of degrees of mixing for some time. Ergodicity is one such description of mixing for which many people have an intuitive feel; roughly, a flow is ergodic if during the course of its evolution every particle comes close to all points in the mixing domain. Although this may sound like "good mixing," in reality it may not be, because we want more than just every particle to explore every part of the domain. We also want points to lose track of each other, to "forget their past." Making these intuitive notions mathematically precise is the province of "smooth ergodic theory," which has developed definitions stronger than ergodicity; one of these is deceptively termed just "mixing," and a still stronger property is called "Bernoulli," which, in some sense, is the strongest possible mixing. Remarkably, it is possible to rigorously prove that LTMs exhibit Bernoulli mixing, and this was established in the late 1970s and early 1980s (*8–11*). However, after this, LTMs were largely forgotten in the dynamical systems community.

It may be time to bring LTMs to the forefront again. Heuristically, and in the simplest picture, chaotic mixing happens when streamline portraits viewed at different times—or, in the case of a channel flow, viewed in the axial direction—show streamline crossing (*7*). Thus, channels can be imagined as being made up of concatenated, alternating "sectional elements"; the droplets are a superposition of two mirror images of two flows. We have shown (*7*) that the fluid particle motion in all of these mixers can be described in terms of an LTM or an appropriate generalization of an LTM.



**Mixer with a twist.** (**A**) Schematic representation of a channel-type micromixer. Streamline patterns are shown at the ends of the mixing element. The details of the shape and internal structure of the channel, the motion of boundaries, and the manner of driving are not shown; they can be anything that produces the desired cross-sectional flow (which defines the family of designs). (**B**) Two blobs shown in the superposition of the outer streamlines in the cross section at the end of each mixing element for a case where the flow features underlying the LTM theorems provide good mixing properties. The integer *n* denotes the number of mixing segments (where a mixing segment is two concatenated mixing elements). The flow appears well mixed after 10 mixing elements. (**C**) The same blobs as in (B), but for a case where the flow features underlying the LTM theorems fail to provide good mixing.

The mixing properties of an LTM depend on the "strength" of the rotations, on whether the rotations are in the same or opposite sense, and on a measure of the "overlap" of the cross-sectional flows at the end of each mixing element (see the figure). If these parameters satisfy certain inequalities and relations in a mathematical theorem (*7–11*), then it follows that the channel mixer has the Bernoulli property. Hence, one only need design the cross-sectional elements so that these properties of the streamlines hold. One could view this as a "design theory" for which the explicit mathematical formulas describing the dynamical system are not the key issue. Rather, dynamical systems are classified according to broad geometrical features that define families of dynamical systems that are qualitatively the same. These results, coupled with computational fluid dynamics capabilities, allow one to "experiment" with different design strategies from a new point of view—combining, for example, the specificity of computational fluid mechanics and the abstraction of LTMs—and permit an evolution through a continuum of possibilities before settling into specifics.

Microfluidic applications can benefit by a closer linkage and use of basic theory. This viewpoint is not new. A prominent report (*12*) in the area of nanotechnology advocates a greater role for modeling and theory. Technology is about design, and design is about convergence. However, converging too quickly without thinking deeply about the global picture may result in suboptimal designs. There are clearly opportunities for work in global aspects of mixing flows from a dynamical systems viewpoint. This is an area where seemingly esoteric work may have a direct impact on the bottom line.

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