

# Experiment Tracks the Progress of a Chaotically Mixed Chemical Reaction

Imaging an electromagnetically stirred tray of chemicals under diverse conditions reveals surprisingly uniform behavior.

If you drop a spoonful of sour cream into a bowl of goulash soup, the two liquids will barely mix. But if you stir them, the spoon will drag filaments of cream through the soup. Stir further, and the filaments will stretch and fold. Eventually, if that's your taste, the cream and soup will blend completely.

How stirring converts a spatially inhomogeneous state into a homogenous one seems like the sort of problem G. I. Taylor might have solved in the 1930s. But only in the past 20 years have the mathematical tools—deterministic chaos and statistical hydrodynamics—become available to build plausible theories.

Those theories have advanced to include components that react with each other. Now, they're being tested in the lab. Paulo Arratia of the University of Pennsylvania in Philadelphia and Jerry Gollub of Haverford College outside Philadelphia have developed an experiment that tracks the progress of a chemical reaction in a stirred solution.<sup>1</sup>

To their surprise, Arratia and Gollub discovered a simple, seemingly universal parameterization that reflects the growth rate of chemical product under a variety of conditions. And, because the parameterization features a mathematical abstraction known as the Lyapunov exponent, it's amenable to theoretical comparison.

Like cream and goulash, Arratia and Gollub's experiment runs in a subturbulent chaotic regime where the kinetic energy is confined to a modest range of length scales. Fully turbulent systems

are far harder to study, but they're more relevant to chemical engineers, who want to mix things as efficiently as possible.

Still, understanding chaotic mixing is of more than academic interest. Slow-moving ocean currents stir and disperse the nutrients that plankton, the fount of the marine ecosystem, feed on. And microfluidic mixers operate in a subturbulent regime because of their small size.

### **Stirred not shaken**

Flows stretch and move fluid elements, thereby increasing the opportunities for the reactants they contain to meet and combine. Diffusion is generally too slow to act as an efficient go-between—which is why one shakes test tubes and stirs goulash.

To measure the stretching, Arratia and Gollub applied a method Gollub developed in 2002 with Haverford's Greg Voth and MIT's George Haller.<sup>2</sup> The method tackles two traditional challenges in fluid dynamics: imaging 3D flow and dealing with boundaries.

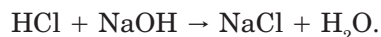
In fact, the setup is 2D. The fluid occupies a shallow square tray, 15 cm wide and 5 mm deep. The fluid's velocity field is measured by imaging the changing positions of  $10^8$  microscopic latex tracers.

To create a velocity field in the first place, one needs to shake the container or stir the fluid. Both methods create troublesome inhomogeneities at the walls of the container or the at edges of the stirrer. Voth, Haller, and Gollub solved the boundary problem by using electromagnetism. They make the fluid electrically conducting and position the tray on top of an array of 30 or so magnets. Applying a periodic electric field across the tray drives the fluid back and forth over the magnets. Lorentz forces do the stirring. Arranging the magnets in a regular or random pattern creates a

more or less symmetric velocity field.

The production rate depends not only on the structure and rapidity of the flow, but also on the reaction time—that is, how quickly the reactants, once brought together, combine chemically. As the fluid elements stretch and fold, their interfaces, where the reaction occurs, fatten and fill with product.

Arratia and Gollub investigated the aqueous acid–base reaction



Because the reacting solution isn't particularly conductive, Arratia and Gollub float it in a thin layer on top of the stirred conducting fluid. The reaction is fast. A typical run would take a second to complete.

At the start of the experiment, the acid and base solutions are kept apart. To monitor the reaction's progress, Arratia and Gollub added a *pH*-sensitive fluorescent dye to the acid. Once the barrier is removed and the electromagnetic stirring begins, the local intensity of the fluorescent signal traces the change of *pH* as acid and base neutralize each other.

### **Lyapunov exponents**

Mixing is more closely related to the stretching and folding of fluid elements than to their velocity. By tracking tracers in their stirred fluid, Arratia and Gollub measured the velocity field. From it, they derived the stretching field—that is, the local distortion of an infinitesimally small fluid element. Figure 1 shows examples of both types of field.

One way to characterize local stretching is through an exponent devised more than a century ago by Alexander Lyapunov. After a time  $\Delta t$ , two originally adjacent fluid elements separate by a dis-

tance  $\exp(\lambda\Delta t)$ , where  $\lambda$  is the Lyapunov exponent. In a laminar flow,  $\lambda$  is zero throughout. In chaotic and turbulent flows,  $\lambda$  varies from point to point.

Arratia and Gollub ran their experiment for a range of Reynolds numbers and magnet arrangements. And they plotted how  $P$ , the total amount of chemical product, increased as a function of various quantities, including  $N$ , the number of times the electric field was switched back and forth and  $\lambda$ , the field-averaged Lyapunov exponent.

As expected,  $P$  increased with both  $N$  and  $\lambda$ . Raising the Reynolds number accelerated the increase, as did arranging the magnets aperiodically rather than periodically. But fluid dynamacists, like other physicists, seek evidence of universal, predictive behavior. In the hope of finding it, Arratia and Gollub plotted  $P$  against various quantities. When they used  $\lambda N$  as the  $x$ -axis, they discovered all their curves collapsed to one. Figure 2 shows the result.

Can theory account for the figure? In a recent paper, Györgi Károlyi of Budapest University of Technology and Economics and Tamas Tél of Eötvös University, which is also in Budapest, applied the techniques of deterministic chaos to the problem.<sup>3</sup> Their analysis, which relies on Károlyi's concept of a time-dependent fractal dimension, predicts that  $P$  should rise as  $1 - \exp(-\alpha\lambda N)$ , where  $\alpha$  is a constant. The model, represented by the blue curve in figure 2, accounts for the data at early times, but fails at later times. The black curve, which has the form  $1 - \exp[-\alpha\lambda N - \beta(\lambda N)^2]$ , fits better, but is purely empirical.

Gollub notes that fluid elements, in addition to being

stretched and folded, can also be transported by flows. Transport, he speculates, could be the missing ingredient that a successful physical model should contain.

**Charles Day**

## References

1. P. E. Arratia, J. P. Gollub, *Phys. Rev. Lett.* (in press).
2. G. A. Voth, G. Haller, J. P. Gollub, *Phys. Rev. Lett.* **88**, 254501 (2002).
3. G. Károlyi, T. Tél, *Phys. Rev. Lett.* **95**, 264501 (2005).

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**Figure 1. When stirred, a thin layer of liquid** develops a velocity field (top row) and a stretching field (bottom row). The magnets responsible for stirring can be arranged either aperiodically (left column) or periodically (right column). (Adapted from ref. 1.)

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**Figure 2. For a diverse range of experimental conditions** (colored dots), the normalized amount of reaction product  $P$  increases at the same rate when plotted against  $\lambda N$ . The black curve is an empirical fit; the blue curve is the model from reference 3. (Adapted from ref. 1.)

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