

do, that the parts-per-million CMB fluctuations in the incredibly homogeneous plasma epoch were the seeds of today's highly structured universe.

As of this writing, NASA's MAP (Microwave Anisotropy Probe) satellite was scheduled for launch at the end of June. From its quasi-stable

perch at the Lagrange point L2, a million miles antisunward from Earth, MAP should be able to measure the CMB power spectrum with unprecedented sensitivity and precision.

BERTRAM SCHWARZSCHILD

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Feedback Tames Chaotic Surface Chemistry

Chaotic systems typically lurch from one point in phase space to another, usually wildly different one. Yet amid the seemingly random flailings, episodes of near periodic behavior appear, then disappear, like spells of sunny weather in storm-battered Shetland.

In their ability to quickly change states, chaotic systems can outmaneuver their incrementally changing linear cousins. But if their nimbleness is to be exploited, chaotic systems must be harnessed and controlled. Paths must be found to the desirable, well-behaved states.

In the early 1990s, the University of Maryland's Edward Ott, Celso Grebogi, and James Yorke proved theoretically that a chaotic system can indeed be controlled.¹ Now known as OGY, their method is to apply judiciously chosen perturbations to an available system parameter. (For more on controlling chaos, see Ott and Mark Spano's article in *PHYSICS TODAY*, May 1995, page 34.)

Since that pioneering effort, which was first brought to bear on a wobbling magnetoelastic ribbon,² various chaotic systems have been tamed—among them, oscillatory chemical reactions. In these bizarre systems, two or more reactions wax and wane in turn as each inhibits and promotes the other. With the right mix of conditions, the concentrations of species in chemical oscillators can be induced to exhibit temporal chaos or, in some cases, spatiotemporal chaos.

The first chemical oscillator to be controlled was the classic Belouzhov-Zhabotinsky (BZ) system of reactions. Discovered 50 years ago, the BZ system involves a somewhat complex mix of reactants, but it boils down to a simple plan. A slow reaction consumes a species that stifles a second, faster reaction that can be switched on autocatalytically.

As it proceeds, the fast reaction triggers the production of the species that inhibits it, and the cycle begins again. With the right mix of concentrations, the BZ system oscillates chaotically.

With a single parameter as a tiller, surface scientists can steer a model catalyst away from chaos toward regimes of regular, repeating behavior.

The state of the BZ system can be monitored by dipping an electrode into the vat of reactants and measuring the reactions' ionic fluctuations. In 1993, Kenneth Showalter's group at West Virginia University used a perturbation method akin to OGY to successfully control temporal chaos in a BZ system.³

Now, from Harm Hinrich Rotermond's group at Berlin's Fritz Haber Institute (FHI), comes an experiment that extends the control of chemical chaos in a significant and new direction.⁴ Working with a simple catalytic system, the FHI team created chaotic spatiotemporal patterns of surface reactants and then, by using a simple feedback mechanism, pushed the system into one of several well-behaved, nonchaotic spatiotemporal regimes.

"It's a major advance in understanding and controlling complex spatiotemporal behavior," says Showal-

ter. What's more, the chemical system that the FHI group studied—the oxidation of carbon monoxide on platinum—is an idealized version of what goes on in the catalytic converters of cars and trucks. It's closer, therefore, to practical applications than the rather academic BZ system.

Lifted reconstruction

In their experiments, the FHI researchers waft CO and O₂ in a vacuum over the (110) surface of a single Pt crystal. When O₂ molecules hit the surface, they dissociate into two O atoms that stick firmly to the surface. CO molecules also stick to the surface, but, being more loosely bound, diffuse about.

When a CO molecule encounters an O atom, the two combine to make a carbon dioxide molecule, which promptly leaves the surface. In a car's catalytic converter, this reaction converts the poisonous CO to the less malign CO₂.

Two key phenomena cause the CO-O-Pt system to oscillate: asymmetric inhibition and lifted reconstruction. Asymmetric inhibition occurs because CO needs just one adsorption site, whereas the dissociating O₂ needs two adjacent sites. If too much CO covers the Pt surface, oxidation can't occur. At that point, the catalyst is, as chemists say, "poisoned."

Reconstruction is the rearrangement of surface atoms with respect to the bulk. It occurs no matter how the surface is created. In the case of Pt(110), surface atoms rearrange themselves in such a way that every second row is missing.

When CO coverage reaches about half a monolayer—the point at which poisoning occurs—CO removes (or "lifts," as surface scientists say) the reconstruction, restoring the bulk configuration to the surface. This is significant because oxygen's sticking probability is 50% higher for the bulk configuration.

Asymmetric inhibition and lifted reconstruction work together to produce an oscillation as follows. Start off

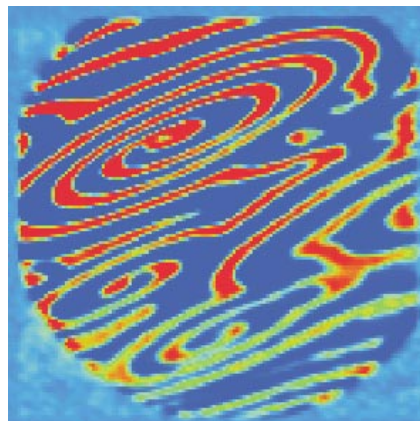


FIGURE 1. CHAOTIC SPIRALING patterns of carbon dioxide and oxygen can form on a platinum surface. In this snapshot from a photoemission electron microscope (PEEM), red represents the areas of the Pt surface covered in carbon monoxide; areas covered by atomic oxygen are shown in blue. The field of view is 500 μm across. (Adapted from ref. 4.)

with two fixed pressures of CO and O₂ such that the CO coverage builds up. When the coverage approaches half a monolayer the reconstruction of the Pt(110) surface lifts, abruptly increasing oxygen's sticking probability. More oxygen is adsorbed; more CO reacts with it to form CO₂, which then desorbs, reducing the CO coverage and restoring the surface to its reconstructed state. We're now back where we started, ready for another cycle.

The CO-O-Pt system produces spatiotemporal patterns because one of the key actors in the process, the CO molecule, diffuses about the surface. From cycle to cycle, a CO molecule typically diffuses 10–50 μm.

To study the patterns, the FHI team uses a photoemission electron microscope (PEEM). This instrument illuminates the surface with ultraviolet light, provoking the emission of photoelectrons, whose flux depends on the local work function. "An oxygen-covered surface has a higher work function than a CO-covered surface, so it emits fewer photoelectrons," explains Minseok Kim (now at Northwestern University), who did most of the FHI experiments.

By recording the intensity, location, and arrival time of the photoelectrons, the PEEM produces a movie (at 25 frames a second) of the surface patterning. But the PEEM doesn't just monitor the surface. It also provides the information for controlling the patterning. The trick is to adjust the instantaneous partial CO pressure $p(t)$ by an amount that depends on the integrated PEEM intensity I measured τ seconds earlier.

The method is called global delayed feedback: "global" because $p(t)$, which actually controls the chaos, depends on I , which is integrated over the whole surface; "delayed" because $p(t)$ depends on $I(t - \tau)$, rather than $I(t)$.

Mathematically, $p(t)$ is given by

$$p(t) = p_0 + \mu[I(t - \tau) - I_0].$$

Here, p_0 and I_0 are base levels of CO partial pressure and integrated PEEM intensity, respectively. The strength of the feedback is given by μ , the parameter that, with τ , determines the feedback process.

Figure 1 shows what happens if chaos is unchecked. Compare it with

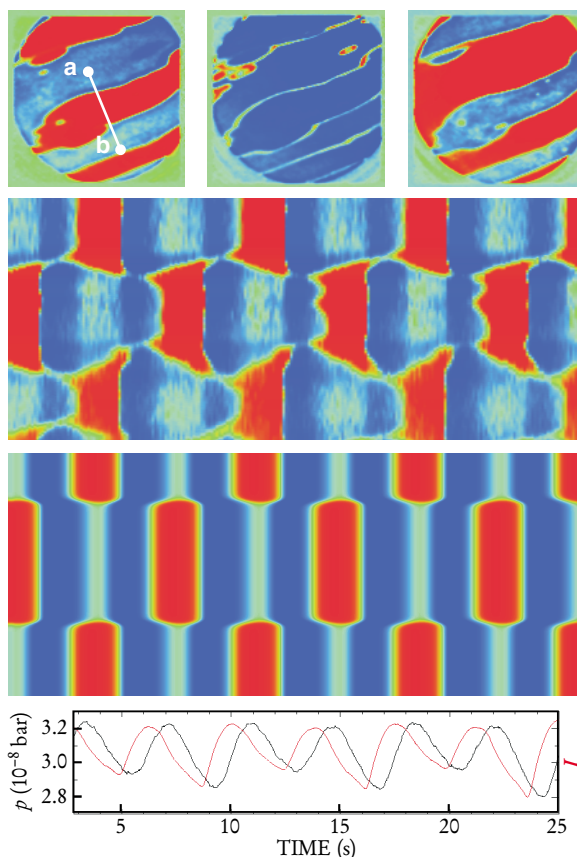


FIGURE 2. "PHASE CLUSTERS" is the name nonlinear dynamicists give to the sort of spatiotemporal patterns shown here. The first row consists of a set of three snapshots from the photoemission electron microscope (PEEM) taken during the course of the experiment. The line from *a* to *b* in the upper left identifies a thin section of the surface, whose evolution is shown in the second row. This image is made up of thin vertical strips, each of which shows the state of surface section *ab* at successive 50-ms instants. The third row is a numerical simulation of the patterns shown in the second row. The bottom row has the same time axis as the second and third rows. The red line tracks the integrated PEEM intensity I , which acts as the input for adjusting the partial pressure p (the black line) of carbon monoxide. These adjustments are responsible for controlling the surface chemistry to maintain the spatiotemporal pattern. (Adapted from ref. 4.)

figure 2, where the initial values of the two partial pressures were such that spatiotemporal chaos would ordinarily have ensued. However, applying the feedback (with τ set at 0.8 s and μ at 6×10^{-9} bar) forced the system into a regime of stable oscillating stripes.

The FHI group didn't stumble on the global delayed feedback method by chance. Rather, the method was first suggested in 1996 by Alexander Mikhailov, who heads FHI's complex systems group, and Dorjsuren Battogtokh, who was visiting the group at the time (he's now at Kyoto University).

With the Ginsburg–Landau equation as their principal analytic tool,

these two theorists discovered that nonlinear dispersion in distributed dynamical systems could be controlled by global delayed feedback. And with numerical simulations, they demonstrated what sort of patterns were obtainable.

One such simulation, done by Mikhailov and FHI's Matthias Bertram, appears in figure 2 below the experimental data. The resemblance is striking. However, the experimental system is very sensitive to the values of τ and μ . Says Kim, "The theoreticians predicted what I might see, so I had a rough idea of what to expect. But I had to find the real parameters by trial and error."

Complete control

Global delayed feedback does not require extensive computation to implement. This is an advantage over methods, such as OGY, that entail constructing maps in dynamical space and calculating a trajectory to reach the desired state.

But on the debit side, global delayed feedback falls short of providing complete control. Rather than charting a course to an arbitrarily chosen end state, the method makes it possible to consistently achieve one of several end states that can be predicted more or less in advance.

Rotermund foresees using the feedback method to optimize the course of surface reactions. He's particularly interested in reactions that have two products: one desirable the other undesirable. "By doing this feedback loop and watching the surface, you can increase the selectivity for the product that you want," he says.

The method could also be applied to surface reactions that work only on the circumference of circular islands. Adjust the partial pressure and you shrink or grow the island, influencing the outcome of the reaction. "That's a pretty sure thing," says Rotermund. "At least we believe it is!"

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