

Chemical gardens grown in flatland

R. Mark Wilson

Citation: *Physics Today* **68**(1), 14 (2015); doi: 10.1063/PT.3.2641

View online: <http://dx.doi.org/10.1063/PT.3.2641>

View Table of Contents: <http://scitation.aip.org/content/aip/magazine/physicstoday/68/1?ver=pdfcov>

Published by the [AIP Publishing](#)



Cuts that remove part of a lattice are allowed, for instance, but only if subsequent folding and bond reformation around the excised area can restore the lattice's connectivity without altering the bond lengths.

Panel a in the figure shows one of the group's prototypical kirigami templates. The hole at the center can be closed only with a specific set of folds—along the dotted lines—that cause parts of the surface to pop out of the plane, as shown in panel b. So-called mountain folds (M) mark the perimeters of the raised plateaus; valley folds (V) mark the perimeter of the basin.

Kamien and his colleagues find that cut-and-fold sequences can be characterized by the topological defects they leave behind. Any sequence giving rise to a 3D feature will necessarily create disclinations, sites at which the lattice symmetry is disrupted. In the figure, for instance, the mountain and valley folds converge on pairs of cells having five (yellow) and seven (green) neighbors, instead of the usual six. Known by condensed-matter theorists as Stone–Wales defects, those pairs and their associated folds are encoded by V-shaped cuts—dubbed five–seven cuts and highlighted in blue in panel a—that each bisect adjacent edges on the lattice.

While experimenting with paper templates, Xingting Gong, an undergraduate student in Kamien's lab, discovered a second kind of kirigami cut that creates a pair of vertices having two and four neighbors instead of three. That so-called two–four cut, also V-shaped, runs along adjacent edges instead of bisecting them. The resulting plateau is taller and more sharply angled than that of the five–seven cut.

Kamien's postdoc Toen Castle deduced that the two–four and five–seven cuts are the fundamental building blocks from which all allowable kirigami structures derive. In essence, that's because folds can preserve lattice distances only if the angle of the associated cut is an integer multiple of an angle of rotational symmetry. The two–four and five–seven cuts are, respectively, the minimum-angle cuts satisfying that criterion for the honeycomb's three- and sixfold rotational symmetries. By cleverly mixing and matching those cuts, one can design kirigami templates that fold into boxes, staircases, and other shapes.

In real systems, if the energy gained by repairing a lattice's bonds exceeds the energy costs of folding it, a kirigami template can be self-assembling. Recent simulations suggest that kirigami might

be useful for fashioning self-assembling graphene containers for hydrogen storage or for manipulating mechanical and electronic properties in graphene-like materials.²

Kamien thinks, however, that from a technical standpoint kirigami might be more easily applied to systems having larger length scales, such as DNA assemblies. For instance, DNA origami can be used to shape genetic material into tiles that then self-assemble into 2D periodic lattices.³ Kirigami could provide a means to coax those lattices into drug delivery capsules, nanomachine parts, and other 3D structures.

Because unwanted material is snipped away at the outset, kirigami in principle permits the fabrication of

more complicated structures—from fewer, simpler folds—than can be made with origami alone. The Penn group is now working to devise algorithms to exploit that feature. Says Kamien, “How do you make something that pops up into, say, a pyramid, using as little material as possible? Now that we have a basic framework, we can begin tackling those kinds of questions.”

Ashley G. Smart

References

1. T. Castle et al., *Phys. Rev. Lett.* **113**, 245502 (2014).
2. S. Zhu, T. Li, *ACS Nano* **8**, 2864 (2014); Z. Qi, H. S. Park, D. K. Campbell, <http://arxiv.org/abs/1407.8113>.
3. C. Geary, P. W. K. Rothmund, E. S. Andersen, *Science* **345**, 799 (2014).

Chemical gardens grown in flatland

When certain inorganic reactions are confined to a two-dimensional cell, the mineral precipitates conform to a simple geometric model.

In 1646 chemist Johann Glauber dropped a crystal of ferrous chloride (FeCl_2) into a solution of potassium silicate (K_2SiO_3) and within minutes saw

“philosophical trees,” the name he coined for the plant-like shapes that emerged during the reaction. More than three and a half centuries later, sci-

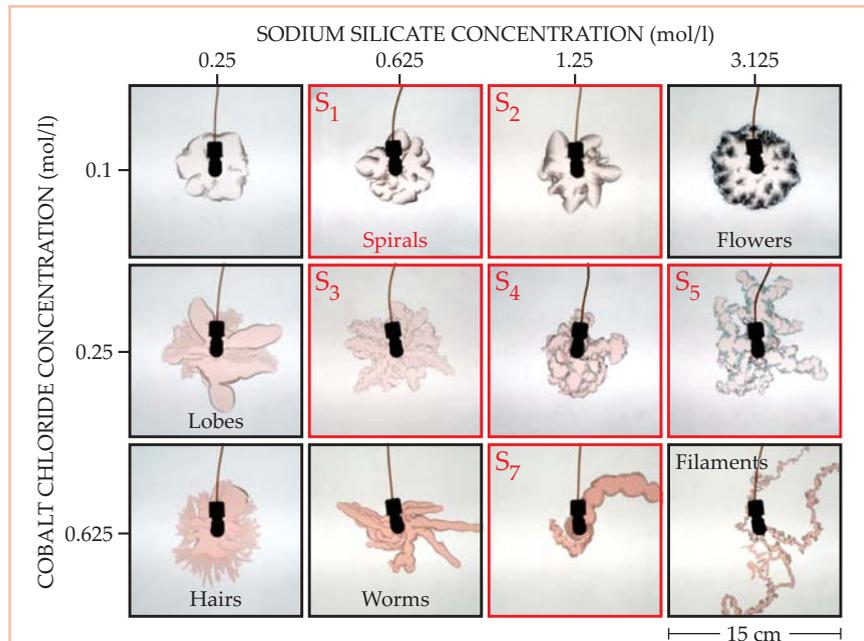


Figure 1. A gallery of quasi-two-dimensional chemical gardens. A solution of cobalt chloride, one of the typical metallic salts used to grow a 3D chemical garden, is introduced through the silhouetted injector at a rate of 0.1 ml/s into a reservoir of sodium silicate that fills the half-millimeter gap between two transparent plates. Each snapshot was taken 15 s after the injection began an experiment. As the concentrations of silicate and salt vary between experiments, so do the emergent patterns of mineral precipitates. Patterns labeled S_i feature spiral shapes on closer inspection, as shown in figure 2. (Adapted from ref. 2.)

entists still only qualitatively understand how the mineral scapes, now known as chemical gardens, grow into their rich variety of structures. Making them could hardly be simpler: Precipitates are produced when a metal salt dissolves in an alkaline solution of anions, such as silicate, phosphate, or carbonate. That simplicity makes chemical gardens a popular and dramatic demonstration among high schoolers. The science behind the drama, though, is not so simple.

As the salt crystal dissolves, it becomes enveloped in an insoluble semipermeable membrane of the solid metal silicate. Osmotic pressure pulls water from the outside to the inside and further dissolves the salt. The membrane inflates, eventually ruptures, and releases a buoyant jet of metal-rich inner solution that rises and precipitates a new membrane in the outer solution. The result, once the salt is dissolved, is a self-assembled aggregate of hollow mineral stalks. But their growth, driven by a complex interplay between osmosis, buoyancy, reactions, and diffusion, is highly nonlinear and difficult to reproduce from one experiment to the next.

In 2003, to reduce the reaction's complexity, Florida State University's Oliver Steinbock led a study that replaced the solid metal salt and instead injected one liquid solution at a constant rate into a beaker full of another.¹ The step, which led to the first systematic experiments on the gardens' tubular growth, not only avoids the erratic effects of dissolution but gives researchers control over the concentration and viscosity of each reagent as the semipermeable membranes repeatedly form and rupture.

Anne De Wit at the Free University of Brussels (ULB) in Belgium, Julyan Cartwright of the Spanish National Research Council, and their colleagues Florence Haudin and Fabian Brau, both also at ULB, have now further constrained the reaction.² Like Steinbock, they injected one solution into another—specifically, cobalt chloride into a reservoir of sodium silicate or vice versa. But they did so using the quasi-two-dimensional geometry of a Hele-Shaw cell, in which the reservoir sits in the half-millimeter gap between two horizontal acrylic plates. The confinement effectively eliminates the buoyancy force.

Precipitation patterns

The confinement also makes the system mathematically tractable. In particular,

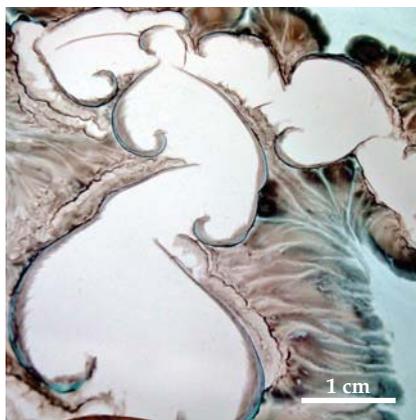


Figure 2. Spiraling precipitates grow diffusively out of the semipermeable membranes that form a two-dimensional chemical garden when a solution of cobalt chloride (pink) is injected into and reacts with colorless sodium silicate in a confining cell. This snapshot, from experiment S_3 in figure 1, was taken a few minutes after the end of the injection. (Adapted from ref. 2.)

the Hele-Shaw cell's planar geometry allows one to replace the formidable 3D Navier-Stokes equations with a simplified set of linear equations to describe the flow. The geometry confers experimental advantages as well. By mounting a video camera atop the transparent cell and a light pad below it, the researchers monitored the reaction's progress *in situ*.

The new approach offers reproducibility among identical experimental conditions. But despite the constraints imposed by their 2D system, the researchers found a surprising plethora of patterns—spirals, lobes, worms, flowers, filaments, and others—when they systematically varied either the injection rate or, as shown in figure 1, the reagent concentrations.

A general trend was for precipitation patterns to become circular if one reagent is much more concentrated than the other. When Na_2SiO_3 is used at its highest concentration, for example, it is an order of magnitude more viscous than CoCl_2 at its lowest concentration, and the precipitate accumulates at the outer rim as the dark petals of a flower. The petals emerge as viscous fingers, the hydrodynamic response to the instability that occurs whenever a less viscous fluid is pumped into a more viscous one (see PHYSICS TODAY, October 2012, page 15). When the concentrations of both reagents are high, the precipitates grow into long, meandering filaments. When the concentrations

JANIS

From ARPES to X-ray Diffraction



Janis has **cryogenic research equipment** to help with your application. Our engineers will assist you in choosing the best system for your requirements.

Contact us today:
sales@janis.com

www.janis.com/Applications.aspx
www.facebook.com/JanisResearch

of both are low, wide lobes emerge instead.

To explore a pattern common to 2D gardens—and discernable in some 3D ones—De Wit and her colleagues analyzed the growth kinetics of 173 curly-shaped precipitates they observed in several experiments (marked S_1 in figure 1). The shapes, shown more clearly in the magnified view of S_3 in figure 2, were pervasive throughout a wide range of intermediate concentrations. And all of

the curls conformed to the mathematics of a logarithmic spiral—the logarithmic dependence of angle on radius—the same structure found in natural systems such as seashells, snail shells, and the horns of animals. In the case of their experiments, De Wit says, “what matters is to have a solid that is pushed, breaks, and starts to rotate when material is added in a self-similar way at the end of a propagating tip.”

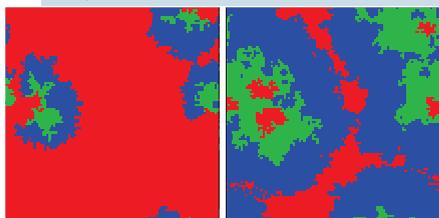
Cartwright adds that so generic a

model—independent of chemical details—is merely a first step to quantifying how the 2D system behaves. “We’re hoping to model other features, such as the filaments, which are reminiscent of the stalks, or tubes, in 3D gardens, to further constrain the growth mechanism,” he says. A detailed and quantitative 2D model would surely provide some insight and predictive power over the behavior of 3D gardens and such natural formations as deep-ocean hy-

physics update

These items, with supplementary material, first appeared at <http://www.physicstoday.org>.

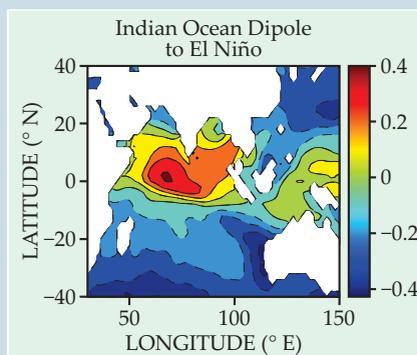
The cost and benefit of deception. Imagine the police arrest you and a colleague for some crime and offer individual deals if you will betray each other. If only one of you defects, that person goes free while the other, the cooperator, receives three years in prison. Mutual defection gets both of you a two-year sentence, and mutual cooperation results in a one-year sentence. That game theory scenario is called the prisoner’s dilemma. Versions of it, often involving many players who adapt their strategies as they repeatedly play the game, have been used to study how cooperative behavior might evolve in a population of competing individuals. Now Attila Szolnoki of the Hungarian Academy of Sciences and Matjaž Perc of the University of Maribor in Slovenia and King Abdulaziz University in Saudi Arabia have introduced deception to the game. They ran Monte Carlo simulations with up to 3.6×10^7 players interacting on a square lattice. In addition to defectors,



the simulations included conditional cooperators who defect if they detect a defecting opponent, and deceptive defectors who always avoid detection, though at a cost. After playing against its four neighbors, a player could switch strategies depending on how well it did in comparison to the previous player; a randomly chosen neighbor then went next. The figure above shows snapshots from one simulation after 60 (left panel) and 100 (right panel) Monte Carlo steps; the population of cooperators (blue) grew at the expense of defectors (red), but in turn lost ground to deceptive defectors (green). The researchers found that such complex dynamics led to surprising evolutionary outcomes. For example, deception sometimes became more effective when its cost increased, and upping the likelihood of detection didn’t always promote cooperation. (A. Szolnoki, M. Perc, *New J. Phys.* **16**, 113003, 2014.)

—SC

Quantitative causality. Cause and correlation are two different notions that are often confused. When phenomena A and B are causally related, their time evolutions are correlated. But correlation does not imply causality—an external agent such as an alarm clock, for example, can cause the correlated waking of two sleepers; the two isolated wakings, however, are not causally related. When the dynamics governing A and B are known, an information-theoretic notion called



information flow rigorously determines the causal relations between A and B : If the information flow from A to B is zero, A has no effect on B ; otherwise, A does affect B . Now X. San Liang of the Nanjing University of Information Science and Technology in China has shown how to obtain the information flow, not from *a priori* known dynamics but from correlations in the time-series graphs that detail the evolutions of A and B . He applied his result to a problem of practical interest for climate scientists—the relation between El Niño and the Indian Ocean Dipole (IOD), an aperiodic oscillation in sea surface temperature. Liang used correlations between time series—of sea surface temperatures in the Indian Ocean and of an index, called Niño4, that measures the overall strength of El Niño—to calculate the information flow from the IOD to El Niño shown in the figure. For a large swath of the northern Indian Ocean, the sign of the information flow is positive, which, according to information theory, means the IOD causes El Niño to be less predictable. That unusual causal link, suggests Liang, may be the reason climate scientists only recently recognized an influence of the IOD on El Niño. (X. S. Liang, *Phys. Rev. E* **90**, 052150, 2014.)

—SKB

Detecting shielded uranium in the field. Security personnel use several methods to detect suspect materials such as explosives and dangerous chemicals (see *PHYSICS TODAY*, June 2014, page 62). But uranium—especially the highly enriched weapons-grade version—can be difficult to spot because it is easily shielded by a relatively small amount of lead, which absorbs the fissile material’s telltale emissions. However, neutrons directed at a suspect object can readily penetrate the lead shielding and produce enough fission neutrons and gamma rays to be detected. For field operations, small and light neutron sources are needed. Jennifer Ellsworth and a team of researchers at Lawrence Livermore National Laboratory (LLNL) have developed a suitcase-sized prototype neutron source that they say can be shrunk to a 5-kg, 20-W, lunchbox-sized device that could be easily transported to inspect a suspicious item. Central to the device is an array of 40 etched iridium tips (in the assembly at left in the figure). The 100-nm-radius tips concentrate the electric field from a com-

drothermal vents, rust tubes emanating from corroded iron or steel, and hollow, briny icicles under Arctic sea ice.

De Wit and her colleagues see another compelling application for their approach: building new complex materials. By turning to a catalog of patterns or phases like the one in figure 1, researchers may be able, De Wit speculates, to control the reaction well enough to produce the desired pattern and complexity. But that's a goal for the

long run. And it may involve other building blocks. A related class of self-assembling mineral aggregates known as silica biomorphs also exploits steep pH gradients like those found in chemical gardens—though using a different mechanism—to assemble leaf-like sheets, helical filaments, and “cauliflowers” (see PHYSICS TODAY, March 2009, page 17).³

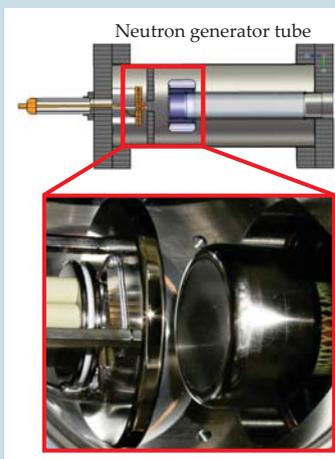
Possibilities abound. It's intriguing to imagine, for instance, a filament-rich

chemical garden, tailor-made using an appropriately tweaked recipe, operating as a microfluidic delivery system or catalytic filter.

Mark Wilson

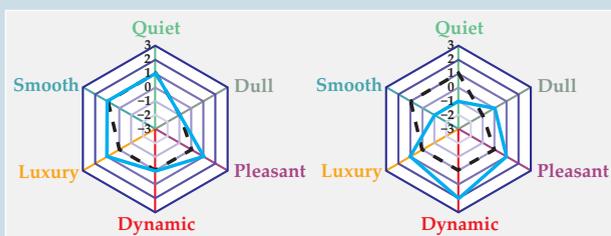
References

1. S. Thouvenel-Romans, O. Steinbock, *J. Am. Chem. Soc.* **125**, 4338 (2003).
2. F. Haudin et al., *Proc. Natl. Acad. Sci. USA* (in press), doi:10.1073/pnas.1409552111.
3. See also W. L. Noorduin et al., *Science* **340**, 832 (2013).



compact 10- to 20-kV power supply; the concentrated field rips apart and ionizes the molecular deuterium gas near the tips. Impinging on a tritiated-titanium target (at right) that is biased to -100 kV, a pulsed D^+ current of 120 nA in the prototype generates bursts of 10^7 14-MeV neutrons, a flux that is an order of magnitude higher than was previously available in field-ionization neutron sources. The team's prototype has produced D^+ currents up to 500 nA while consuming less than 10 W. The LLNL team is bringing the size and weight down and the output up, which will allow neutron analysis to join portable x-ray devices in the field of nondestructive materials interrogation. (J. Ellsworth et al., *J. Appl. Phys.* **116**, 193301, 2014.) —SGB

Sound design for electric vehicles. The interior of an electric vehicle can sound eerily quiet without the noise of a combustion engine, yet also annoying due to unfamiliar, high-frequency sound components. Options for introducing virtual sounds are boundless, but as Soogab Lee and colleagues at Seoul National University show, psychoacoustics and musical harmonic theory can offer guidance. Both loudness and sharpness, which is related to the proportion of high-frequency components, can negatively affect pleasantness. To enhance the dynamic impression, the researchers wanted the sounds to correlate with speed. Harmonious



engine sounds, whose frequencies are in simple integer ratios, have been found to be more pleasant, so the Seoul team focused on tones harmonically related to the car interior's dominant high-frequency component during acceleration. The researchers had 27 volunteers evaluate five combinations of added tones (available online) by rating their overall im-

pression and then describing the sounds in terms of attribute pairs “pleasant–unpleasant,” “calm–dynamic,” “smooth–rough,” “loud–quiet,” “sharp–dull,” and “luxury–cheap.” As shown by the figure's blue lines, two of the five were rated higher for luxury and pleasantness than the base sound (dashed line) and were more preferred overall. For the combination rated on the left (the fourth audio sample), the original and added tones had the frequency ratio 5:3:1, reminiscent of a clarinet. The other (the third sample), with subharmonics that were three and four octaves below the original, was deemed rougher and louder but more dynamic. That combination was particularly favored by the dozen testers who like their cars “sporty.” (D. Y. Gwak et al., *J. Acoust. Soc. Am.* **136**, EL391, 2014.) —RJF

Extragalactic Rydberg atoms. The cold neutral medium (CNM) is one of the most enigmatic components of interstellar space. Conditions that prevail in the low-temperature, low-density CNM are such that carbon atoms are more likely to be ionized than the more abundant hydrogen atoms. And when those atoms recombine with ambient electrons, they can form fragile, high-quantum-number Rydberg states whose initial deexcitations entail the emission of low-energy photons. Photons from those deexcitations have now been seen outside our galaxy for the first time. Leah Morabito of Leiden University in the Netherlands and her collaborators found them in the nearby star-forming galaxy M82; they used LOFAR, an array of about 20 000 radio dipole antennas centered in a field outside the Dutch village of Exloo. LOFAR can barely detect individual Rydberg transitions in M82. But by stacking the spectra of 22 transitions from quantum numbers 468–508 down to the next lowest state, Morabito and her colleagues obtained an 8.5-standard-deviation detection. For this proof-of-concept observation, only LOFAR's central 2-km core was used (see figure). Although the core couldn't resolve M82's structure, the stacked spectrum's profile suggests that the origin of the carbon absorption lies in the vicinity of the galaxy's star-forming nucleus. Future observations with the full array will pinpoint the carbon's location. The discovery of extragalactic Rydberg absorption opens a new window on the CNM, which LOFAR's more sensitive successor, the Square Kilometer Array, is poised to exploit when it debuts next decade. (L. K. Morabito et al., *Astrophys. J. Lett.* **795**, L33, 2014.) —CD

