Entropy and order work together in an artificial spin ice

The very factor that propels most of the universe toward disorder pushes an array of nanomagnets into a visibly ordered state.

Students of thermodynamics learn that closed systems tend toward states of increasing entropy, which is often considered synonymous with decreasing order. But in some systems, entropy and order can be allies, not opponents: The systems tend toward greater order as—and precisely because—their entropy increases.

The phenomenon isn't as paradoxical as it sounds. The secret is to partition the system's degrees of freedom into two subsets, so that ordering in one subset increases the entropy of the other—and thus of the system as a whole. The trick is well known in soft-matter physics, where entropy-driven order shows up in contexts such as colloidal crystallization: When an ensemble of particles assembles from a disordered dispersion into an ordered lattice, each one can have more room to move around.

The mechanical motion of colloidal particles involves continuous degrees of freedom, which can be complicated to model and difficult to precisely measure. Now Yale University's Peter Schiffer, Los Alamos National Laboratory's Cristiano Nisoli, and their colleagues have shown that entropy-driven order can also occur in an array of nanomagnets called an artificial spin ice—a system whose degrees of freedom are solely discrete.[1]

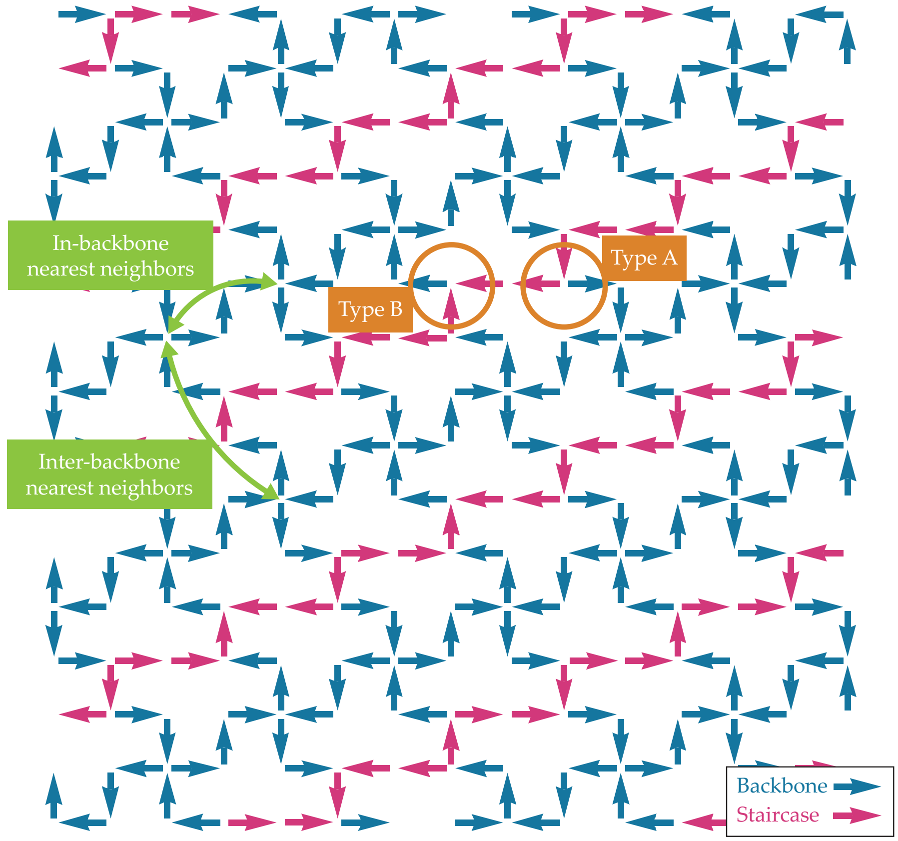

FIGURE 1. TETRIS ICE, an array of nanomagnets outlining a tessellation of T-shaped tetroids, is a vertex-frustrated system. Although the lowest-energy state for the three-way vertices is the one labeled "type A," a global arrangement of moments must have some vertices in the higher-energy "type B" state. Because of the many ways of arranging the type-A and type-B vertices, the lattice—and in particular, the set of staircase moments, shown in pink—has a large residual entropy. The staircase entropy drives the backbone moments, shown in blue, to adopt a large-scale alternating pattern, not just among in-backbone nearest neighbors but also among inter-backbone nearest neighbors. (Adapted from ref. 3.)

Ice degeneracy

Artificial spin ices are designed to mimic natural spin ices, which, in turn, take their name from water ice. The salient common feature of all three classes of systems is that the internal interactions can be frustrated to prevent the system as a whole from having a unique low-energy ground state. Instead, they can relax into any one of a vast number of nearly energy-degenerate configurations.

In water ice, each H_2O molecule sits at a tetrahedral vertex in one of six possible orientations: Each of the two hydrogen atoms can point toward any one of the four neighboring molecules. Because no two H atoms can point toward each other, positioning one molecule restricts the possible orientations of its neighbors, but not enough to fully fix the global configuration. An ice crystal therefore has residual entropy, even at absolute zero.

Natural spin ices are compounds with a similar tetrahedral lattice structure, but with magnetic spins in place of H-atom positions. The system seeks to lower its energy by balancing the spins pointing toward and away from each vertex. But that criterion isn't enough to guide the spins toward a single ground state.

With water ice and natural spin ices, researchers are limited to studying the structures that nature provides. But with artificial spin ices, they're free to create any lattice structure they want. (See the article by Ian Gilbert, Cristiano Nisoli, and Peter Schiffer, Physics Today, July 2016, page 54.) They can therefore design systems where residual entropy not only is present but gives rise to unusual emergent phenomena.

Vertex frustration

Schiffer, Nisoli, and colleagues' spin ice of choice in the new work, which they call "tetris ice," is shown in figure 1. Each of the blue and pink arrows marks the position of an oblong nanomagnet whose

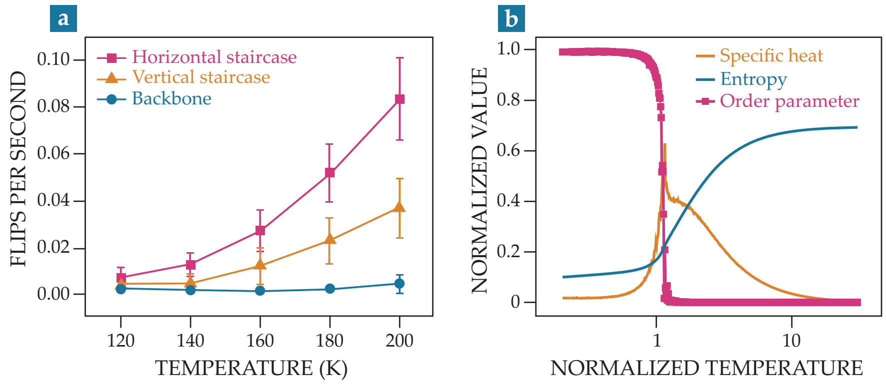

FIGURE 2. ENTROPY-DRIVEN ORDER in tetris ice can be studied in quantitative detail. **(a)** Imaging of the system over time shows that the staircase moments, where the lattice entropy is concentrated, change their magnetization much more frequently than the backbone moments, which are driven toward order. **(b)** A Monte Carlo simulation exhibits an order–disorder phase transition, despite the system's residual entropy at low temperature. (Adapted from ref. 1.)

magnetization is free to point in either of two directions along its length. Like natural spin ices, artificial spin ices can lower their energy by equalizing the number of moments pointing into and out of each vertex. If a vertex has more than one moment pointing in (or out), the lowest-energy state is the one that maximizes those moments' angular separation.

A vertex where four magnets meet has a clear lowest-energy state—with alternating moments pointing in and out—that's adopted in one of two possible configurations by all of the four-way vertices in the figure. A three-way vertex, on the other hand, can't have equal numbers of moments pointing in and out. Its lowest-energy state, labeled "type A" in the figure, is the one where the collinear moments either both point in or both point out. The "type B" state, with one of the collinear moments pointing in and one pointing out, is slightly higher in energy.

The important property of the tetris-ice lattice, as Nisoli and colleagues pointed out in a theory paper in 2013, is that it's vertex-frustrated: There's no way to arrange the moments so that every vertex is in its lowest energy state.[2] In practice, nearly all of the higher-energy vertices are type B three-way vertices. But the system has many ways to allocate its three-way vertices to type B and type A.

The sections of the lattice shown in blue, which the researchers call "backbones," have no three-way vertices, so each one can (and usually does) settle into its lowest-energy state, with the four-way vertices alternating in configuration. If that alternating pattern extends across multiple backbones—that is, if both in-backbone nearest neighbors and inter-backbone nearest neighbors have alternating configurations—then the staircases in between, shown in pink, have many ways to arrange their type B vertices that are all fairly low in energy. But when the backbones break the antiferromagnetic pattern, so that inter-backbone nearest neighbors have the same configuration, then the intervening staircase is limited to just one low-energy state.

Nisoli and his theory colleagues teamed up with Schiffer's group to study the system experimentally. For magnets a few hundred nanometers long, the energy barrier to spontaneously reversing magnetization is close to the room-temperature thermal energy. Furthermore, it's possible to quickly and reliably probe the magnet's states using x-ray magnetic circular-dichroism photoemission electron microscopy, so the experimenters can watch and record the system's configuration as it evolves over time.

In a 2016 paper, the joint team observed that tetris ice could be well described as a series of quasi-one-dimensional backbones and staircases, and they described the staircase behavior in terms of the 1D Ising model.[3] After that, the system sat on the back burner until 2020, when the COVID-19 lab closure prompted the researchers to reexamine old data in search of new understanding.

Data and theory

Many questions remained about the

tetris-ice system. With the backbones separated by staircases, which had so many available energy-degenerate configurations, can the backbones correlate with one another, and if so, by what mechanism? On the other hand, if tetris ice is really a composite of isolated 1D chains, that would seem to imply that it, like the 1D Ising model, could never undergo an order–disorder phase transition at any finite temperature.

Hilal Saglam, then a postdoc in Schiffer's group and now at Princeton University, took charge of sorting through the accumulated data. She found that although the backbone moments were more sluggish to flip than the staircase moments (as shown in figure 2a), the backbones did tend to organize into ordered antiferromagnetic domains—not just in one dimension but in two.

Nisoli's team proposed the ordering mechanism. Whenever two neighboring backbones broke the antiferromagnetic pattern, the staircase in between didn't pay an energy penalty, but it did pay an entropy penalty because of the fewer available low-energy configurations. The system's free energy—energy minus entropy times temperature—is therefore higher for the disordered-backbone state. Because systems tend to lower their free energies, the staircases' entropy drives the backbones toward order.

The smoking gun for that explanation would be to start with all the backbones completely out of antiferromagnetic order—with all pairs of inter-backbone nearest neighbors having the same moment configuration—and show that they still evolve toward order. Reversing the magnetization of an entire backbone would seemingly take a coordinated effort. Would the force of entropy-driven order be enough to accomplish it?

Unfortunately, experimental spin-ice tools, although adept at measuring a system's configuration, aren't up to the task of initializing the nanomagnets in such a specific state. The scenario the researchers had in mind could be studied only by simulation. Nisoli's postdoc Ayhan Duzgun (now at Intel) developed and refined a Monte Carlo model to match the experimental behavior. Along the way, he confirmed that the tetris-ice dynamics really were governed entirely by the vertex energies, not by any long-range interactions.

With the Monte Carlo simulations, Duzgun explored the system's phase diagram. As shown in figure 2b, it exhibits the hallmarks of an order–disorder phase transition—a spike in the specific heat and a jump in the antiferromagnetic order parameter—that would be impossible in a 1D system. As expected, the entropy never goes to zero, even at low temperature. And sure enough, when the lattice was initialized in a disordered-backbone state, it evolved toward order.

New designs

With their discovery of entropy-driven order in tetris ice, Schiffer, Nisoli, and colleagues now have a foothold to explore other systems in which it might also be lurking. "We're interested in these artificial spin ices to generate new unexpected phenomena that might be harder to find in real materials," explains Schiffer. Because the structure of artificial spin ice is fully under the researchers' control—and limited only by their imagination—they can tune the behavior to be as simple or as complex as they like. One item on their to-do list is to try to generate entropy-driven order in a lattice with more types of geometrically distinct vertices.

The long-term hope is that artificial spin ices could lead to new clues about other systems in which order arises spontaneously in ways that aren't fully understood, up to and including the nanomachinery of life. Even now, artificial spin ices are being explored as platforms for information storage and new modes of computing that may mimic the workings of the human brain. Nisoli can easily imagine entropy-driven order's relevance: "In information theory, entropy represents the uncertainty of an outcome," he says. "But here, it drives a correlation among bits. It makes the outcome more certain."

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References

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