

Crushing a Solution of Left-Handed and Right-Handed Crystals Breaks Its Chiral Symmetry

A simple tabletop experiment could have profound implications for the origin of life.

As the number of atoms in a molecule increases, so does the number of ways of arranging the atoms in space. Of those arrangements, called structural isomers, by far the most numerous are chiral. Such isomers have a definite handedness and can't be superposed on their mirror images.

Given the preponderance of chiral isomers, it's not surprising that all the amino acids in our bodies except the simplest, glycine, are chiral. What's remarkable, however, is that naturally occurring amino acids share the *same* chirality. Although the homochirality of biomolecules astonished Louis Pasteur, who discovered the trait in 1848, its existence does make sense. To function, a protein must reliably adopt a unique complex and distinct three-dimensional shape. Building homochiral proteins from homochiral amino acids serves that goal.

It's harder to understand how homochirality ever arose in the first place before life began. Energetically, left-handed and right-handed isomers are identical and should form with the same probability. A random mix of left-handed and right-handed isomers would be roughly fifty-fifty and any fluctuations in the number N of one isomer would be on the order of $\sqrt{N}$.

The unlikelihood of breaking chiral symmetry by chance has led to some

rather exotic proposals, including the intervention on Earth of circularly polarized light from beyond the solar system. But now, Cristobal Viedma of Complutense University in Madrid, Spain, has shown that an initially equal mix of chiral crystals in solution can achieve complete homochirality thanks to the mundane action of grinding and stirring the crystals.¹

Chiral crystals are not as biologically relevant as chiral molecules. Even so, an essential step in the origin of life now seems less mysterious.

Sodium chlorate

Pasteur made his discovery by examining the action of molds that eat only one chiral isomer of a residue found in wine barrels. In later years, as the field of organic chemistry matured, the extent of homochirality in nature became known. Hormones, enzymes, and DNA are all homochiral. But it wasn't until 1953 that a plausible scheme for the origin of homochirality appeared. In a landmark paper, Charles Frank described a theoretical system consisting of two chiral isomers.² One isomer, the left-handed one, say, catalyzes its own production and at the same time suppresses the production of its right-handed twin.

In thermodynamic equilibrium, an equal mix of such isomers wouldn't

necessarily attain homochirality. But, argued Frank, if the system were far from equilibrium, an initially tiny and random preponderance of one chiral isomer over the other could set off a nonlinear chain reaction. Complete homochirality would ensue.

Frank couched his idea in abstract terms. He had no actual chemical system in mind, but there are some that break other, nonchiral symmetries. In 1951, Boris Belousov discovered that a mix of certain autocatalytic chemicals would, if kept far from chemical equilibrium, oscillate continuously in waves. Anatol Zhabotinsky continued Belousov's work on the now-famous reaction that bears their names.

In the late 1980s, Dilip Kondepudi of Wake Forest University in North Carolina wondered if he could find a system that breaks chiral symmetry as the Belousov-Zhabotinsky reaction breaks translational and temporal symmetries. Kondepudi consulted chemists, who recommended some candidate molecules, but he found the molecules too troublesome to work with.

As a simpler alternative, the chemists suggested sodium chlorate. In aqueous solution, sodium chlorate's Na^+ and ClO_3^- ions are not chiral, but the crystals they form are. The chirality manifests itself in how the crystals transmit light. If linearly polarized light passes through it, the crystal will rotate the angle of polarization left or right, depending on the crystal's chirality. As figure 1 shows, the crystals also change color when viewed through a polarizer.

Left by itself, a solution of sodium chlorate would precipitate roughly equal numbers of left-handed and right-handed crystals. But back in 1898, Frederick Kipping and William Pope discovered that if they dropped a single seed crystal into a supersaturated solution, all subsequent crystals shared the same chirality.

Of course, using an already-homochiral seed can't account for the emergence of homochirality itself. Kondepudi tried to find an achiral stimulus

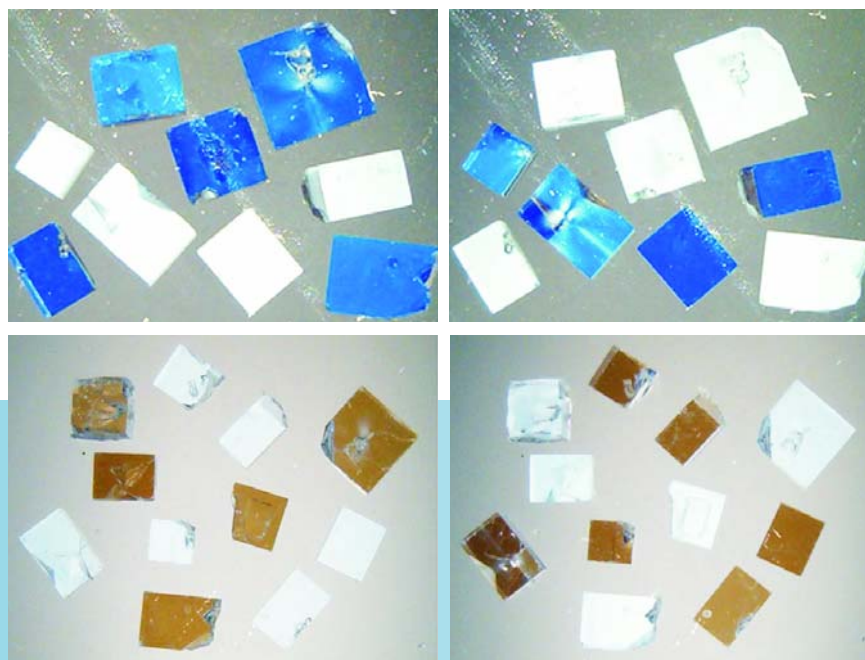


Figure 1. To determine chirality, sodium chlorate crystals are placed on top of a linear polarizer and viewed through a second, initially crossed polarizer. When the crossed polarizer is rotated clockwise, right-handed crystals appear blue. When the polarizer is rotated counterclockwise, left-handed crystals appear red. (Courtesy of C. Viedma.)

that would trigger symmetry breaking. One day, when he was watching a crystal form, he noticed it fall to the bottom of the flask. On a whim, he stirred the solution. To his astonishment, the stirring caused all subsequent crystals to adopt the same chirality as the original crystal. He and his colleagues Rebecca Kaufman and Nolini Singh submitted a paper to *Science*. One of the referees promptly repeated the experiment and obtained the same result. The paper appeared in 1990.³

Secondary nucleation

Kondepudi explained his results in terms of primary and secondary nucleation. In primary nucleation, crystals emerge from solution at a rate proportional to $\exp[-A(T)/\ln^2(c/c_0)]$. Here, $A(T)$ is a function that depends on the temperature T , c is the concentration, and c_0 is the saturation concentration. Left-handed and right-handed crystals have the same chance of forming.

In secondary nucleation, solute crystallizes on the surface of an existing crystal. Newly added material assumes the chirality of the surface.

In the 1990 paper, Kondepudi sketched out the sequence of events. First, a single crystal forms via primary nucleation. In doing so, the crystal reduces the concentration of solute and, with it, the likelihood of further primary nucleation. Stirring the solution increases the likelihood of secondary nucleation, both by bringing more solute into contact with the crystal and by breaking off newly crystallized material to form additional nucleation sites. If no further primary nucleation occurs, all the crystals share the first crystal's chirality.

Secondary nucleation is well known to chemical engineers, who've developed phenomenological rate equations for it. But a physical theory in terms of quantities such as temperature or Boltzmann's constant is lacking. After Kondepudi's paper ap-



peared, various workers, including Kondepudi himself, tried to quantify how stirring promotes secondary nucleation. Does contact with the stirrer matter? Does convection—that is, stirring without a stirrer—produce the same results?

Last year, Julian Cartwright of the Spanish Research Council realized that stirring, contact with the bar, convection, and so on were all doing the same thing on the microscale: breaking off the tiny whiskers that sprout from crystals when they form. In a paper published last year, Cartwright and his collaborators demonstrated the idea in a mix of theory, computation, and experiment.⁴

Viedma has added a new twist. In Kondepudi's and Cartwright's experiments, the starting point is a solution devoid of chiral entities. Viedma started instead with a supersaturated solution that contains a fifty-fifty mix of chiral crystals. Like Kondepudi, he stirred the solution, but in the presence of glass marbles (see figure 2). Crushed between the marbles, any crystals that have just formed are broken down. Meanwhile, others form and the cycle repeats—but not

Figure 2. A metal bar, controlled electromagnetically, forces crystals between glass beads and breaks them up. At the same time, new crystals form. Eventually chiral purity results. (Courtesy of C. Viedma.)

in a chiral steady state.

Viedma found that if he left his samples grinding away for several hours, one chiral form would steadily predominate. The dominant form was random, but the result was the same: complete chiral purity.

To understand the results, one needs to add another ingredient: Ostwald ripening. In 1896, Wilhelm Ostwald observed that big crystals grow at the expense of little crystals thanks to the big crystals' greater thermodynamic stability. In Viedma's experiment, one would expect left-handed and right-handed crystals to grow and dissolve at the same rate. But if there's a slight, chance preponderance of one chiral form, then Ostwald ripening, amplified by secondary nucleation, will shift the chiral balance.

Viedma's experiment, though it converts an achiral mixture into a homochiral one, is still a far chemical cry from chiral amino acids or the origin of life. But five years after Kondepudi's 1990 experiment, Kenso Soai of the Tokyo University of Science in Japan demonstrated that he could guide the homochiral formation of an organic molecule by recruiting the help of sodium chlorate crystals.⁵ Inorganic chiral crystals, Soai points out, were around when life began.

Charles Day

References

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First Experiment at National Ignition Facility Focuses on Hydrodynamics of Plasma Jets

Supersonic jets generated by shock waves are common, on vastly different scales, to high-energy astrophysics, inertial-confinement-fusion targets, and nuclear weapons.

As big as a football stadium, the National Ignition Facility (NIF), under construction at Lawrence Livermore National Laboratory, is scheduled for completion in 2009. The \$3.5 billion undertaking will serve an im-

pressive variety of users. When focused on a millimeter-size capsule filled with tritium and deuterium, NIF's 192 laser beams will be able to heat and squeeze it with a 2-megajoule, nanosecond pulse of light (see

the cover of this issue). As the facility's name implies, such a pulse is thought to be powerful enough to ignite a thermonuclear burn in the hydrogen-isotope mix.

The NIF project is administered by the Department of Energy's National Nuclear Security Administration, which oversees the stockpile stewardship program for ensuring the reliability of the nation's nuclear arsenal