

## **Unexpected 'Black Swan' defect discovered in soft matter for first time**

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In new research, Texas A&M University scientists have for the first time revealed a single microscopic defect called a "twin" in a soft-block copolymer using an advanced electron microscopy technique. This defect may be exploited in the future to create materials with novel acoustic and photonic properties.



"This defect is like a black swan—something special going on that isn't typical," said Dr. Edwin Thomas, professor in the Department of Materials Science and Engineering. "Although we chose a certain polymer for our study, I think the twin defect will be fairly universal across a bunch of similar soft matter systems, like oils, surfactants, biological materials and natural polymers. Therefore, our findings will be valuable to diverse research across the soft matter field."

The results of the study are detailed in the *Proceedings of the National Academy of Sciences (PNAS)*.

Materials can be broadly classified as hard or soft matter. Hard materials, like metal alloys and ceramics, generally have a very regular and symmetric arrangement of atoms. Further, in hard matter, ordered groups of atoms arrange themselves into nanoscopic building blocks, called <u>unit cells</u>. Typically, these unit cells are comprised of only a few atoms and stack together to form the periodic crystal. Soft matter can also form crystals consisting of unit cells, but now the periodic pattern is not at the <u>atomic level</u>; it occurs at a much larger scale from assemblies of large molecules.

In particular, for an A-B diblock copolymer, a type of soft matter, the periodic molecular motif comprises of two linked chains: One chain of A units and one chain of B units. Each chain, called a block, has thousands of units linked together and a soft crystal forms by selective aggregation of the A units into domains and B units into domains that form huge unit cells compared to hard matter.

Another notable difference between soft and hard crystals is that structural defects have been much more extensively studied in hard matter. These imperfections can occur at a single atomic location within material, called a point defect. For example, point defects in the periodic arrangement of carbon atoms in a diamond due to nitrogen impurities



create the exquisite "canary" yellow diamond. In addition, imperfections in crystals can be elongated as a line defect or spread across an area as a surface defect.

By and large, defects within <u>hard materials</u> have been extensively investigated using advanced electron imaging techniques. But in order to be able to locate and identify defects in their block copolymer soft crystals, Thomas and his colleagues used a new technique called sliceand-view scanning electron microscopy. This method allowed the researchers to use a fine ion beam to trim off a very thin slice of the soft material, then they used an electron beam to image the surface below the slice, then slice again, image again, over and over. These slices were then digitally stacked together to get a 3D view.

For their analysis, they investigated a diblock copolymer made of a polystyrene block and a polydimethylsiloxane block. At the microscopic level, a unit cell of this material exhibits a spatial pattern of the so-called "double gyroid" shape, a complex, periodic structure consisting of two intertwined molecular networks of which one has a left-handed rotation and the other, a right-handed rotation.

While the researchers were not actively looking for any particular defect in the material, the advanced imaging technique uncovered a surface defect, called a twin boundary. At either side of the twin juncture, the molecular networks abruptly transformed their handedness.

"I like to call this defect a topological mirror, and it's a really neat effect," said Thomas. "When you have a twin boundary, it's like looking at a reflection into a mirror, as each network crosses the boundary, the networks switch handedness, right becomes left and vice versa."

The researcher added that the consequences of having a twin boundary in a periodic structure that does not by itself have any inherent mirror



symmetry could induce novel optical and acoustic properties that open new doors in materials engineering and technology.

"In biology, we know that even a single defect in DNA, a mutation, can cause a disease or some other observable change in an organism. In our study, we show a single twin <u>defect</u> in a double gyroid material," said Thomas. "Future research will explore to see whether there's something special about the presence of an isolated mirror plane in a structure, which otherwise has no mirror symmetry."

**More information:** Xueyan Feng et al, Visualizing the double-gyroid twin, *Proceedings of the National Academy of Sciences* (2021). DOI: 10.1073/pnas.2018977118

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