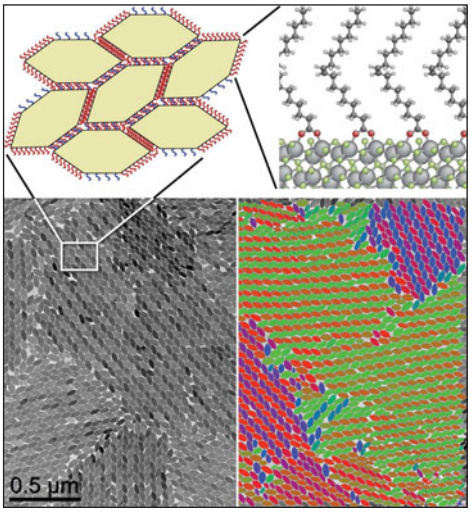
Nano Focus

"Interaction patchiness" leads to herringbone nanocrystal pattern

The programmed assembly of crystalline nanoparticles into large-scale superlattices promises the ability to construct materials with tailor-made properties. However, the ability to control the packing of nanocrystals with defined morphologies is only beginning to be realized. A mystery that has remained elusive is why some sets of nanocrystals arrange themselves in an alternating, herringbone style instead of the expected tiled patterns. Now a team of researchers from the University of Pennsylvania, the University of Michigan, the Massachusetts Institute of Technology, and Intelligent Material Solutions, Inc., in Princeton has found an answer, as reported in the online edition of *Nature Chemistry* (DOI: 10.1038/NCHEM.1651).



Rare-earth flouride nanoplates self-assemble at the liquid–air interface into the herringbone pattern.

By exploiting the differences in packing of oleic acid ligands around nanoparticles with well-defined facets, which leads to an "interaction patchiness," the researchers have succeeded in generating unique ordered assemblies of nanoparticles. Sharon Glotzer, the Stuart W. Churchill Collegiate Professor of Chemical Engineering at Michigan, introduced the concept of "patchiness" in 2004, and her group uses computer simulations to understand and design the patches.

Recently, her group was approached by Christopher Murray's group from the University of Pennsylvania. Murray's team made patterns with flat lanthanide fluoride nanocrystals, whose surfaces were functionalized with oleic acid. These particles have sizes of ~100 nm and by using lanthanides with different atomic radii, the researchers could control the morphologies of the nanoparticles to be anywhere between hexagonal and diamond-shaped.

The diamond shapes and the very long hexagons lined up as expected, the diamonds forming an Argyle-style grid and the hexagons matching up their longest edges like a foreshortened honeycomb. The hexagons whose sides were all nearly the same length should have formed a similar squashed honeycomb pattern, but instead, they lined up in a more complicated, alternating herringbone style.

"Whenever we see something that isn't taking the simplest pattern possible, we have to ask why," said Murray, the Richard Perry University Professor and professor of chemistry.

They posed the question to Glotzer's team.

Glotzer and her group built a computer model that could recreate the self-assembly of the same range of shapes that Murray had produced. They found that if the edges that formed the points were stickier than the other two sides, the hexagons would naturally arrange in the herringbone pattern. The teams suspected that the source of the stickiness was the carbon and hydrogen chains, which may attach to the point edges more easily.

Ju Li's group at the Massachusetts Institute of Technology calculated how the chains would attach to the edges at a quantum mechanical level. The team confirmed that because of the way that the different facets cut across the lattice of the metal and fluorine atoms, more hydrocarbon chains could stick to the four edges that led to points than the remaining two sides. As a result, the particles become patchy leading to the herringbone arrangement.

Glotzer said, "Our study shows a way forward making very subtle changes in building block architecture and getting a very profound change in the larger self-assembled pattern."

Bubbles in metallic glass facilitate fracture

Bubbles in champagne in a glass may add a festive fizz to the drink, but microscopic bubbles that form in metallic glass can signal serious trouble. In this normally high-strength material, bubbles may indicate that a brittle breakdown is in progress.

That's why researchers at Johns Hopkins University used computer simulations to study how these bubbles form and expand when a piece of metallic glass is pulled outward by negative pressure, such as the suction produced by a vacuum. Their findings were published in the May 3 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.110.185502).

"A lot of people are interested in metallic glasses because of their strength and their potential use to make better cell phone cases, computer housings and other products," said Michael L. Falk, who supervised the research. "But what precisely causes these materials to break apart or 'fail' has remained a mystery. By studying the behavior of the bubbles that appear when these glasses crack, we were able to learn more about how that process occurs."

The nearly random arrangement of atoms gives metallic glasses distinctive mechanical and magnetic properties. Most metallic glasses are reasonably elastic and often spring back to their original shape after being bent. Still, when a powerful enough force is applied, they can break.

"Our lab team is interested in learning just how susceptible metallic glasses are to fracturing and how much energy it takes to create a crack," said Falk, a professor in the Whiting School of Engineering's Department of Materials

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