Understanding nanostructure formation from building blocks

A series of theoretical experiments shows how the shape of a particle can generate a specific structure.

THE GROWING USE OF NANOTECHNOLOGY IN LUBRICATION is leading to the development of improved performance in a number of applications. This column has highlighted how researchers are developing new nanoadditives and new nano-based lubricants that display superior properties.

For example, as reported in a previous TLT article, researchers developed a more effective transformer oil with the assistance of hexagonal boron nitride nanoparticles.[1] The reason that this nanoparticle type was used is because it displays good electrical insulation properties in combination with good thermal conductance. At a treat rate of 0.1%, the hexagonal boron nitride nanoparticles helped to boost thermal conductivity by approximately 80%.

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KEY CONCEPTS

- A series of theoretical experiments show how specific particles can arrange themselves into particular crystalline structures.
- Of the 145 different polyhedral shapes studied, only 44 do not self-assemble into an ordered structure.
- The isoperimetric quotient and the coordination number correlate to predict the general class of structure that will form from a given particle shape.

Another area where nanotechnology has been extremely useful is in catalysts, which are widely used in the manufacture of additives, base oils and synthetic lubricant basestocks. A previous article discussed the development of a more stable zeolite nanocatalyst.[2] Prior attempts to prepare zeolite nanocatalysts have not succeeded due to either destruction of the crystal structure or aggregation. Researchers prepared a more functional zeolite nanocatalyst through the use of a solid-state exfoliation process.

These two examples demonstrate the importance that a specific structure has in dictating or controlling performance at the nanoscale. What if a process could be developed to predict the type of crystal structure that can be formed based on the shape of a specific particle?

Progress toward that goal was achieved as recently reported in *Science*.[3] Team Leader Sharon Glotzer, Stuart W. Churchill Collegiate Professor of Chemical Engineering and Material Science and Engineering at The University of Michigan in Ann Arbor, Mich., says, "Nanoparticle building blocks that have specific shapes want to fit together to form certain crystalline structures. With the large number of different possible geometries and crystal types, it is very challenging to correlate a specific building block with a particular structure."

The number of crystal structures range from regular crystals, such as the cubic structure that characterizes sodium chloride, to more complex crystals isomorphic (e.g., gamma brass) and liquid crystals that are used in electronic applications such as flat-screen televisions and computer monitors. Plastic crystals exhibit a degree of disorder with particles literally spinning in place. Finally, a quasicrystal structure has been identified where order is seen locally, but without periodicity over a larger range.

Glotzer says, "If a process can be created to show how the general shape of a particle can generate a specific structure, then the experimental work and time needed to produce such a structure will be reduced. One of our goals is to develop a means to conduct predictive design."

Work has now been done to show how specific particles can arrange themselves into particular crystalline structures.

THE ROLE OF ENTROPY

Glotzer and her research associates conducted a series of theoretical experiments using a thermodynamic Monte Carlo simulation to predict how structures assemble from specific particle shapes. She says, "The Monte Carlo technique is a workhorse tool, especially useful in studying soft materials and complex fluids. In our study, we evaluated 145 different polyhedral shapes including Platonic, Archimedean, Catalan and Johnson solids."

The study was very extensive and took over a year to complete. Glotzer adds, "We generated an extraordinary amount of data." The structures seen were organized into periodic and aperiodic crystals, liquid crystals, plastic crystals and disordered glassy phases.

Of all of the polyhedral shapes studied, only 44 did not self-assemble into an ordered structure during the time scale of the simulations. Glotzer comments, "We do not know why, for these 44 shapes, crystallization is either difficult or unachievable, so this remains an objective for us to figure out in the future. The polyhedra appear to form a glassy state that does not have discernible rotational or translational order."

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Figure 2 shows one example of a crystal structure formed from a five-sided pyramid (four "sides" plus a base).

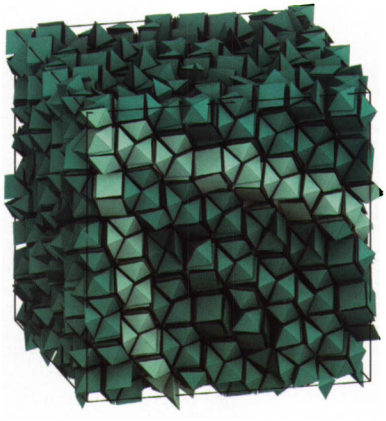

Figure 2 | **New research provides insight into how shapes such as a five-sided pyramid can form the crystal structure shown.** *(Courtesy of The University of Michigan)*

The researchers used the isoperimetric quotient and the coordination number in the fluid phase to predict the type of crystal that will form. The former is a measure of the ratio of a polyhedron's volume to that of a sphere with the same surface area, and the latter is a measure of the preferred number of particles around a specific particle while still in the fluid phase.

Glotzer says, "These two quantities correlate to predict, for the first time, the general class of structure that will form from a given particle shape. No such correlation was previously known."

Entropy plays a key role in predicting how these hard particles can arrange themselves into ordered structures. Equilibrium thermodynamics dictates that systems of particles attain the lowest possible free energy state. Although traditionally entropy is thought of as leading to disorder, it can order nanoparticles in the absence of other interactions.

Glotzer explains, "The role of entropy in self-assembly of ordered structures is counterintuitive to ways of thinking about entropy. For a box filled with 20% particles, there is a tendency for disorder because there is so much empty space. But when the box becomes crowded with many particles (e.g., above 50%), the particles arrange to maximize the amount of space or "wiggle room" each particle has, and this can be achieved through ordering.

Another way to look at this phenomenon is to imagine all of the squares of a checkerboard are occupied with checkers. Rather than being stationary, each of the checkers moves randomly within its own square contributing entropy to the system, thus stabilizing the structure. Glotzer says, "This entropic ordering process is well known for hard spheres, rods and disks, but our simulations show that it can be exploited for a wide range of particle shapes."

Future work for Glotzer will involve development of a predictive theory and software packages for materials design. This means that in the future if a specific lubricant structure is needed for a particular application or use case, then a theory and accompanying software could be available to help a researcher predict the type of particle that will be needed to form that structure on the nanoscale.

Additional information on this research can be found by contacting Glotzer at **sglotzer@umich.edu.**

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