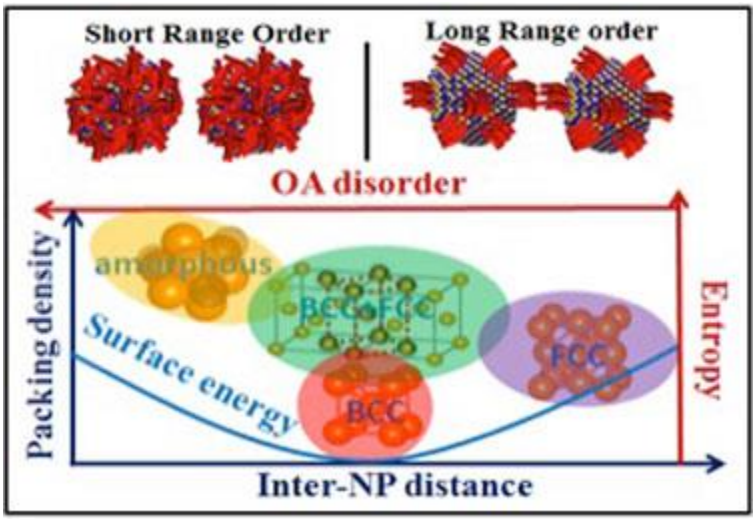
How do superlattices grow?

A team of scientists from Cornell University in the US, the Max Planck Institute of Colloids and Interfaces in Potsdam in Germany, and the University of Hamburg, also in Germany, are the first to have studied how superlattices form. Superlattices are a new class of functional materials made up of assemblies of nanoparticles and could find use in a range of electronics applications, but the structures are still difficult to fabricate in large quantities and in a controlled way.



Supercrystal structure changes

Nanoparticles can be assembled into periodically ordered superlattices that show promise for a range of technology applications, such as photovoltaics, light-emitting diodes and thermoelectrics (TE). However, researchers still do not fully understand how the particles come together via complex nucleation and other processes.

In the early stages of nucleation, nanoparticles aggregate randomly and form an amorphous structure with limited short-range ordering. The particles then minimize the total free energy in the structure by crystallizing into a long-range ordered superlattice. The nanoparticles appear to behave like hard spheres, packing together to form a fairly simple superlattice phase. However, they also appear to go through various, quite intricate nucleation and growth steps that involve multiple nanoparticle interactions with surface-capping ligands and surrounding solvents.

To better understand these mechanisms, the US-Germany team decided to look at how oleic acid capped lead sulphide nanoparticles just 3.5 nm in size assemble in

solution under a wide variety of experimental conditions and different temperatures and pressures. The atomic structure changes occurring at the nanoparticle cores and at the capped ligands can be followed from the same volume of sample using both high-resolution synchrotron small-angle (SAXS) and wide-angle X-ray scattering (WAXS) – new techniques developed by the researchers themselves.

Different polymorphs

The results show that the nanoparticles nucleate in three main superlattice polymorphs: amorphous; body-centred-cubic (bcc); and face-centred-cubic (fcc) phases. The type of superlattice formed can be controlled by changing the distance between the nanoparticles, without touching their size. For example, when the inter-nanoparticle distance is increased, the particles pack together slightly looser but in a more ordered way, and the capping molecules rearrange and change structure, modifying the overall surface energy.

“Our analyses have shown that the nanoparticles appear to either maximize entropy or minimize the enthalpy in the structure so as to reduce the total free energy through multiple interactions with the surface molecules,” explained team leader Zhongwu Wang. “These findings will hopefully inspire both experimentalists and theorists to consider the importance of surface capping molecules when modelling these superlattice structures. From an applications point of view, our phase diagrams could offer a guide to material fabrication and help make ‘designer’ solids with specific structures, inter-nanoparticle distances and sizes.”

The researchers now plan to look at binary nanoparticles and other more complex nanostructures. “Using techniques only available in our labs at the Cornell High Energy Synchrotron Source (CHESS), we aim at building up a series of structure-property relation diagrams of confined nanoparticles with different sizes and shapes,” Wang told *nanotechweb.org*.

The current work is presented in *Nano Letters*.

About the author

Belle Dumé is contributing editor at *nanotechweb.org*.