Harnessing the possibilities of the nanoworld

September 30 2016

Snow Crystal Landscape. Credit: Peter Gorges

Scientists have long suspected that the way materials behave on the nanoscale – that is when particles have dimensions of about 1–100 nanometres – is different from how they behave on any other scale. A new paper in the journal *Chemical Science* provides concrete proof that this is the case.

The laws of thermodynamics govern the behaviour of materials in the macro world, while quantum mechanics describes behaviour of particles at the other extreme, in the world of single atoms and electrons.

But in the middle, on the order of around 10–100,000 molecules, something different is going on. Because it's such a tiny scale, the particles have a really big surface-area-to-volume ratio. This means the energetics of what goes on at the surface become very important, much as they do on the atomic scale, where quantum mechanics is often applied.

Classical thermodynamics breaks down. But because there are so many particles, and there are many interactions between them, the quantum model doesn't quite work either.

And because there are so many particles doing different things at the same time, it's difficult to simulate all their interactions using a computer. It's also hard to gather much experimental information, because we haven't yet developed the capacity to measure behaviour on such a tiny scale.

This conundrum becomes particularly acute when we're trying to understand crystallisation, the process by which particles, randomly distributed in a solution, can form highly ordered crystal structures, given the right conditions.

Chemists don't really understand how this works. How do around 1018 molecules, moving around in solution at random, come together to form a micro- to millimetre size ordered crystal? Most remarkable perhaps is the fact that in most cases every crystal is ordered in the same way every time the crystal is formed.

However, it turns out that different conditions can sometimes yield different crystal structures. These are known as polymorphs, and they're important in many branches of science including medicine – a drug can behave differently in the body depending on which polymorph it's crystallised in.

What we do know so far about the process, at least according to one widely accepted model, is that particles in solution can come together to form a nucleus, and once a critical mass is reached we see crystal growth. The structure of the nucleus determines the structure of the final crystal, that is, which polymorph we get.

What we have not known until now is what determines the structure of the nucleus in the first place, and that happens on the nanoscale.

In this paper, the authors have used mechanochemistry – that is milling and grinding – to obtain nanosized particles, small enough that surface effects become significant. In other words, the chemistry of the nanoworld – which structures are the most stable at this scale, and what conditions affect their stability, has been studied for the first time with carefully controlled experiments.

And by changing the milling conditions, for example by adding a small amount of solvent, the authors have been able to control which polymorph is the most stable. Professor Jeremy Sanders of the University of Cambridge's Department of Chemistry, who led the work, said "It is exciting that these simple experiments, when carried out with great care, can unexpectedly open a new door to understanding the fundamental question of how surface effects can control the stability of nanocrystals."

Joel Bernstein, Global Distinguished Professor of Chemistry at NYU Abu Dhabi, and an expert in crystal growth and structure, explains: "The authors have elegantly shown how to experimentally measure and simulate situations where you have two possible nuclei, say A and B, and determine that A is more stable. And they can also show what conditions are necessary in order for these stabilities to invert, and for B to become more stable than A."

"This is really news, because you can't make those predictions using classical thermodynamics, and nor is this the quantum effect. But by doing these experiments, the authors have started to gain an understanding of how things do behave on this size regime, and how we can predict and thus control it. The elegant part of the experiment is that they have been able to nucleate A and B selectively and reversibly."

One of the key words of chemical synthesis is 'control'. Chemists are always trying to control the properties of materials, whether that's to make a better dye or plastic, or a drug that's more effective in the body. So if we can learn to control how molecules in a solution come together to form solids, we can gain a great deal. This work is a significant first step in gaining that control.

More information: A. M. Belenguer et al. Solvation and surface effects on polymorph stabilities at the nanoscale, *Chem. Sci.* (2016). DOI: 10.1039/C6SC03457H

Provided by University of Cambridge