

## FOREVER HARD

In 1689, Robert Hooke suggested that the goal of natural philosophy should be an understanding of the properties of things: qualities such as fluidity, density and elasticity. This eminently reasonable suggestion that we systematize knowledge in accordance with the way we experience the material world runs into trouble because nature has no reason to respect our experience. You might imagine, say, that the property of hardness is unambiguous enough: surely we know when something is or is not hard, as seemingly illustrated by the Mohs scale that ranks minerals according to their ability to scratch one another.

But hardness is not, after all, a property to which we can affix a number as we can density. A special issue of the *Journal of Superhard Materials* (32, issue 3; 2010) on theories of hardness not only acknowledges that there is still no universally agreed definition of this property but seems to imply that there is little prospect of one being found. For hardness is a property not of a given material, but of a particular sample and how it is probed.

For example, if hardness can be considered a measure of a material's resistance to localized deformation<sup>1</sup>, then it will in general depend not just on the bulk modulus of a crystal structure, nor even on its shear modulus (which depends on the nature and direction of shear), but also on such things as defects and grain size<sup>2</sup>.

This has made research on hard materials highly tendentious, not just because the conclusions may depend on the definition but because measurements can be hard to reproduce. Yet much rests on those results and their interpretations, because we need hard materials urgently and therefore also crave ways of predicting where to look.

It's far from hopeless, however. Standard experimental measures of hardness usually correlate well with bulk and shear modulus<sup>1,3</sup>, and microscopically with high average bond strength, high density and directionality of bonds, and high number of valence electrons<sup>2</sup>. The chemical nature of the bonding is also important<sup>1-3</sup>. Such clues have pointed to, for example, certain heavy transition metals or particular high-pressure phases of silica. A consideration of deformation mechanisms also suggests that nanocrystallinity can improve hardness<sup>3,4</sup> — but only up to a point<sup>5</sup>.

Some years ago it was fashionable to claim (with justification) that no theory, but only empiricism and intuition, had ever identified a new superhard material (that is, one with a hardness that, by some measure, exceeds 40 GPa). Li *et al.*<sup>6</sup> argue that we should be less dismissive of theory today. They admit that 'substitutional' methods, which replace some elements in known crystal structures



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with others, and which for example promised but have so far failed to deliver the  $\beta$ -C<sub>3</sub>N<sub>4</sub> phase<sup>7,8</sup>, have rather limited power to identify good candidates for synthesis. But *ab initio* methods using global free-energy minimization<sup>2,9</sup> are now sophisticated enough to bear fruit, such as new phases of compounds of carbon, boron and nitrogen. Hardness may be hard to pin down, but that no longer prevents us from prescribing it. □

### References

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### NANOCRYSTAL SUPERLATTICES

# Assembly at liquid interfaces

A liquid/air interface provides an effective platform for organizing thin molecular layers that can be transferred to solid surfaces. It is now shown that liquid-interface assembly is effective for generating extensive membranes of binary nanocrystal superlattices.

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Colloidal nanoparticles can be used like building blocks to form materials that have unique properties. One example is the binary nanoparticle superlattice (BNSL) composed of a bidisperse collection of nanoparticles — that is, one with a mixture

of two different sizes<sup>1</sup>. The BNSL consists of two interpenetrating sublattices of large and small nanoparticles, and the packing of the nanoparticles depends primarily on the ratio of their sizes. Thus it is possible to arrange nanoparticles of nearly any composition in

different ways, simply by changing the size ratio of the particles. In practice, however, the assembly of these structures is not so easy. At present the best methods take several hours to complete, requiring a low-volatility solvent evaporated at a slightly elevated temperature