COHERENT DIFFRACTION

Giant molecules or tiny crystals?

Crystallography and microscopy are alternative pathways for investigating the structure of small objects. More elaborate techniques are needed at length scales where atomic clusters become nanocrystals.

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One of the reasons why nanoscience is such a rich subject is that it explores phenomena occurring at length-scales typical of large molecules and of small lumps of 'bulk' matter for which the physical properties are dominated by the interaction with the surroundings. At these length-scales, investigating the structural properties is particularly challenging, as the samples are usually too large for crystallographic methods and too small for microscopy. On page 308 of this issue, Huang *et al.* report their results on the structure of gold nanocrystals obtained by combining sophisticated hybrid 'lensless imaging' with computer modelling[1]. They measured the intensity distribution around three separate Bragg peaks of a nanocrystal, and fitted them with a three-dimensional atomic resolution parameterization of the structure.

The surface layers of the 3.4-nm nanocrystal studied by Huang *et al.* show a strong contraction of the interatomic spacings between the gold atoms. The principle driving this is the smoothing effect proposed by Smoluchowski in 1941: a prediction that the ion cores of the surface atoms of a metal would be drawn inwards in response to the electrons smoothly spreading out at the boundaries of a crystal. Contractions of the lattice have been widely reported on nominally flat metal surfaces; the present result shows that the trend continues to the edges and vertices of a nanocrystal, where atoms have even lower coordination. The trend between lower coordination and reduced bond length, originally predicted by Pauling, has been upheld.

The results of Huang *et al.*[1] are in complete contrast with those of Roger Kornberg's lab published in *Science* a few weeks earlier[2]. Kornberg and colleagues used traditional X-ray crystallography to determine the atomic-resolution structure of a cluster of 102 gold atoms coated with thiolated organic ligands; there, the breakthrough was the chemical synthesis of sufficiently high-quality clusters such that they could be crystallized from a solvent, which presumably selects identical clusters from an already narrow size distribution (though a mixture of two enantiomorphs was found in the structure, nevertheless). The internal structure of this 1.1-nm diameter gold cluster does not resemble the face-centred-cubic lattice observed by Huang *et al.* in the slightest; instead it is based on a five-fold symmetric packing arrangement, known as a Marks Decahedron[3]; moreover, the surface layers of the Au$_{102}$ cluster are strongly influenced by the formation of a network of Au–S bonds with the thiol ligands, including some interesting S–Au–S 'staple' structures. This results in a mixed Au–S skin of thickness 0.2 nm with lower density and Au–Au bond lengths distinctly longer than those in the bulk, instead of shorter for the bare surface seen by Huang and colleagues[1]. The structure of this skin region is highly complex and very different from models of thiols bound on gold surfaces measured by traditional methods.

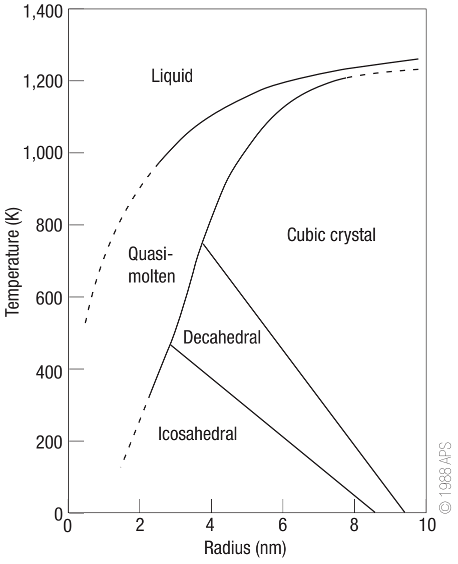

Figure 1 Theoretical phase diagram of the structure of small particles derived in 1988 by Marks[3]. The simple cubic/decahedral/icosahedral sequence of phases is consistent with recent experiments for gold[1,2,4], although the actual position of the boundaries may need adjusting. The strong suppression of the melting point with diminishing size is also consistent with experiment. Reprinted with permission from ref. 8.

This 1.1-nm cluster, which can be thought of as a giant molecule, is one of the largest ever to be crystallized[2]. The tiny 3.4-nm nanocrystal studied by Huang *et al.* is one of the smallest ever to reveal its atomic structure, albeit with some help from the computer modelling[1]. However, we still lack information on particles with sizes between these two extremes, where, going from clusters to nanocrystals, several structural transformations may occur — for example, from a decahedral cluster to a cubic crystal. Electron microscopy of gold crystals has helped establish the notion of a size–temperature phase diagram (Fig. 1), which also features 'quasimolten' and icosahedral phases[3]. In light of these new results[1,2], the position of the phase boundaries may need adjusting, but the order of the phases predicted seems to be correct. In the size range below 4 nm, beam-induced fluctuations in time between cubic and decahedral structures are reported as a function of radiation dose[3], and indeed there is a recent new account of dramatic fluctuations in Au$_{309}$ clusters[4]. To the extent that the beam-induced effects can be considered as a form of heating, these fluctuations are a signature of the 'quasimolten' phase that appears in the phase diagram[3].

Imaging of very small individual particles is generally limited by radiation effects, independently of whether X-rays or electrons are used. The structural fluctuations mentioned above can become an outright explosion of the specimen at higher doses, as the electrons are driven away. Howells has estimated that a maximum resolution of about 10 nm could be achieved for any single object, again using either X-rays or electrons[5]. Crystallography, in which 10^{12} copies of the specimen are imaged in parallel, is one way around the dose problem, but it can only be applied to structures that can be prepared in identical copies; for gold, 102 atoms may be approaching that upper size limit, because of the difficulty of the sample preparation[2].

An alternative for measuring single molecules is X-ray free-electron lasers (XFELs), for the simple reason that the diffraction pattern can be collected more quickly than the radiation damage occurs, thereby defeating Howells' limit. The maximum pulse duration needed to achieve this has been estimated, see for example ref. 6; these estimates (in the range of 20 fs) are within the range expected to be delivered by the XFELs that are currently under construction. It is expected that a single XFEL pulse will contain enough photons to generate a meaningful diffraction pattern, which could be inverted to an image by the methods of Huang *et al.*[1] or else by using some powerful phasing methods originally suggested by Sayre[7].

Materials science at the nanoscale will provide more exciting opportunities for research. The classical view that materials' properties follow from the structure of crystal lattice defects will need revision for structures on the size scale studied by Huang *et al.*[1] and Kornberg and colleagues[2], for which the influence of the surfaces starts dominating over that of the bulk. It is hoped that new modes of defect structure, or patterns of deviation from the bulk, would help us understand why chemical and physical properties are so different in the nanophase.

References

1. Huang, W. J. *et al. Nature Mater.* **7,** 308–313 (2008).
2. Jadzinsky, P. D., Calero, G., Ackerson, C. J., Bushnell, D. A. & Kornberg, R. D. *Science* **318,** 430–433 (2007).
3. Marks, L. D. *Rep. Prog. Phys.* **57,** 603–649 (1994).
4. Li, Z. Y. *et al. Nature* **451,** 46–48 (2008).
5. Marchesini, S. *et al. Opt. Express* **11,** 2344–2353 (2003).
6. Bogan, M. J. *et al. Nano Lett.* **8,** 310–316 (2008).
7. Sayre, D. *Acta Crystallogr.* **5,** 843 (1952).
8. Ajayan, P. M. & Marks, L. D. *Phys. Rev. Lett.* **60,** 585–587 (1998).