Nanoparticle Structure: Going beyond Pictures

Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution,

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Recommended with a commentary by Simon J. L. Billinge, Department of Applied Physics and Applied Mathematics, Columbia University.

Incredible advances in our ability to image and manipulate atoms, such as scanning probe microscopies, gave birth to the ongoing revolution in nanotechnology, capturing the imaginations of scientists and the general public alike. However, to go from imagination to reality we need not just images of nanostructures, but we need to quantify the atomic arrangements giving rise to them. Our traditional methods of crystallography break down on the nanoscale and we don't have robust methods to replace them, something which has been called the "nanostructure problem".

This paper by Kornberg's group at Stanford takes a novel approach to solving the nanostructure problem. Instead of developing a new method for analyzing scattering data from individual nanoparticles (or disordered ensembles of nanoparticles) to give the structure, they solved the problem by managing to crystallize the nanoparticles, then using their existing expertise of protein crystallography to obtain the structure.

In a way this is a boring paper for a physics audience. If anything the breakthrough is in the chemistry of purifying the sample and enticing the crystal to grow. Crystallography was developed by physicists, but the methods used here are routine and were spun off to the chemistry and biology communities a long time ago. So why would I want to highlight the work in a condensed matter physics journal club? In my view this paper is profoundly important to our community. It shows that even simple metallic nanoparticles have a unique structure. They are not just small chunks of fcc material cut out from the bulk. They do not (at least in some cases as here) have some kind of vaguely describable "surface amorphous region". The surface capping layer is not just a bunch of flexible molecules sticking on the surface of a sphere in some non-specific way as the cartoons suggest. The internal structure of the nanoparticles, and the attachments, are unique, reproducible and can be characterized. In short, as with proteins, metallic (and by extension, semiconducting and oxide) nanoparticles can and do have unique structures. The structures are interesting and complex. As the experimental tools for characterizing nanostructures at this

level of quantification and precision develop, the door opens to predicting and designing nanoparticle structures for specific properties, including manipulating nanoparticle surfaces and passivation strategies. Computational physics has a role to play here. Physicists will also continue to play an important role in developing the experimental methodologies for nanostructure characterization, and the study of nanoparticle properties.

As a flavor of this richness, the Kornberg paper describes the structure adopted by what are apparently very stable 102 atom gold clusters capped with 44 p-mercaptobenzoic acid (p-MBA) molecules. The central core is a Marks decahedron (MD), known to be a stable cluster, of 49 atoms, with surrounding gold atoms in well defined positions but in a lower symmetry, and unanticipated, arrangement. At each of the poles of the decahedron (along the 5-fold axis) there are 20 atom clusters that preserve the 5-fold symmetry, but around the equator of the MD the final 13 atoms sit in a ring with no apparent symmetry. This ring imparts a chirality to the structure, so these gold nanoparticles are actually enantiomorphic. Gold atoms in the core have 12 neighbors, as in any close-packed solid and the Au-Au bond lengths vary from 2.8 - 3.1 Å. Gold atoms closer to the surface have fewer neighbors and bind to one or two sulphur atoms on the organic capping molecules with each sulphur binding to two Au atoms.

The details hardly matter. The fact is that nanoparticle structures, even of simple monoelemental noble metal materials, are subtle and rich in their complexity. Being able to characterize them quantitatively, either using protein crystallography or developing alternative novel methods, is the first step in predicting and exploiting these structures for novel properties. Beautiful pictures of nanostructures capture the imagination, but if a *picture* is worth 1000 words, then surely a *table*, filled with accurate atomic coordinates, is worth 1000 pictures as this paper amply shows.