Chemistry 801: *Nanostructured Materials and Interfaces*

Lecture notes: Tuesday Jan. 23

Handouts:

- Syllabus
- Ivan Amato, "Nanotechnology: Shaping the World Atom by Atom"
- Excerpts from Drexler's "Nanosystems: Molecular Machinery, Manufacturing, and Computation," Wiley, 1992

Review of Miller indices (videotape)

There is a political, economic, and social context for nanoscience and nanotechnology. In 2000, the National Nanotechnology Initiative (NNI) became a reality, through the support of Congress and the Clinton administration. In a speech delivered at Caltech, Clinton spoke of the promise of nanotechnology: molecular computers the size of a sugar cube that could store the entire contents of the Library of Congress; and devices that could detect cancerous tumors only a few cells in size and destroy them. The idea of a NNI began with discussions involving the scientific community and various federal agencies. Amato's booklet provides a readable guide to help both scientists and nonscientists understand the implications of this technology, which may well augur the next industrial revolution. The NNI will provide on the order of $0.5B of funding for research in nanoscience and nanotechnology. It is noteworthy that there are also concerns about nanotechnology, some of them articulated in Bill Joy's article in the April, 2000 issue of Wired magazine. Popular fiction is increasingly using nanoscale themes, as in Neal Stephenson's The Diamond Age.

What's special about the nanoscale?

There are three themes that we will encounter repeatedly as we think about science and technology on the nanometer scale. One is that surface effects are accentuated. A second is that scaling laws can break down. The third is that quantum effects can appear.

Amato's article notes the seminal role of a lecture by Feynman, "There's Plenty of Room at the Bottom," which threw down the gauntlet to the scientific community to implement the technical challenges associated with nanoscale miniaturization. Examples in Amato's article of the themes noted above include a "quantum corral," comprising 48 Fe atoms that demonstrates the wave nature of electrons; bioinspired nanomachinery, as in chloroplasts; nanoscale motors driven by ATP; examples of atom imaging and placement; atomically abrupt layers characteristic of semiconductors grown by molecular beam epitaxy; and carbon nanotubes.

Presented below are a number of examples of nanoscale matter and phenomena. These will subsequently be examined in more detail:

1. A stainless steel ball bounces much more elastically on a sample of amorphous metal than on crystalline stainless steel, a consequence of the different nanoscale arrangement of atoms (see movie of this).
2. A liquid sample of ferrofluid, comprising 10 nm ferrimagnetic magnetite particles suspended in oil or water with a surfactant, responds to a magnet (see movie).
3. A reddish sample of gold nanoparticles suspended in aqueous has a completely different appearance than sample of gold foil and illustrates the striking effects of light scattering at this scale. Samples of gold substrates have also been used as platforms for self-assembled monolayers (SAMs) that are bound to the gold through sulfur linkages. This strong chemical interaction between gold and sulfur atoms has been used to link oligonucleotides to nanoparticles of gold for bioassays, as is done by Chad Mirkin at Northwestern.
4. A sample of the elastomer polydimethylsiloxane was shown. This material can be used for soft lithography on length scales approaching nanoscale dimensions.
5. Semiconductor quantum dots and light emitting diodes (LEDs) feature use of nanoscale architecture as a way to control the color and efficiency of emitted light. They are the basis of new kinds for lighting and display technology.

Synthesis is an important consideration in preparing nanomaterials. An example of a top-down approach is the etching of bulk silicon to nanoscale dimensions, porous silicon, which is enormously more luminescent than the bulk solid. An example of bottom-up synthesis is SAM construction.

Surface effects

To look at the dominance of surface effects at the nanoscale, consider a single body-centered cubic (BCC) unit cell like that for Fe. For this cell, there are 8 surface atoms and a single interior atom. If the cube dimensions are doubled so that there are 8 unit cells, there are now 26 atoms on the surface and 9 in the interior. The table below shows that by the time a cube of only five unit cells in each dimension is constructed, there are more interior than surface atoms.

Table 1 Numbers of surface and interior atoms in the BCC structure

Number of unit cells in the cube	Surface (S) atoms	Interior (I) atoms	Ratio (S/I)
1	8	1	8
8 (2x2x2)	26	9	2.9
27 (3x3x3)	56	35	1.6
64 (4x4x4)	98	91	1.1
125 (5x5x5)	152	189	0.8

216 (6x6x6)	218	341	0.6
…			
1,000,000 (100x100x100)	60,002	1,970,299	0.03

Note that for elemental Fe with a unit cell dimension of about 3 Å, cubes less than ~15 Å (1.5 nm) will have a majority of atoms at the surface.