

# Materials and Nanotechnology

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I would like to address three issues in order of increasing generality. I first want to comment on structural chemistry, energetics, and materials in a world that now includes a much greater awareness of phenomena at the nanoscale. This also includes a more general definition, or a more general applicability, of nanomaterials, not just to conventional nanotechnology, but to other areas where the same sort of understanding is essential. The second is to talk about the impact of this work and this sort of thinking on education, particularly at the graduate and postdoctoral level. How do we best take advantage of changing needs to really get people thinking properly? The third is a more general potpourri of societal issues that are with us whether or not we have nanomaterials. These issues are, perhaps, brought to the fore by this latest industrial revolution.

## Nanoscale Science

Let us begin with the science. I am a solid-state chemist and thermodynamicist by training and practice. We are interested in the structure of the solid state and the energies that hold molecules or atoms together in solids. I sometimes say I count calories for a living, for the energetics of materials offers tremendous insight, particularly in a systematic way, into the bonding of atoms and molecules. The energies of phase transitions and chemical reactions whisper of the interatomic forces and bond energies that put atoms and molecules together. The entropies of materials sing of lattice vibrations, of magnetism, of electronic transitions, of order-disorder. These items, put together, determine the sorts of materials that we can have and do have, both in classical and nonclassical ways. An example in the classical equilibrium way is represented by "heat it and beat it" metallurgy and ceramic science, in which the

end product is essentially an equilibrium-phase assemblage; then, in the nonclassical way, the preparative pathway still has to be energetically possible, but the product we obtain is a kinetic result of the pathway and not an equilibrium material. This liberation from the tyranny of equilibrium has led, in part, to the nanotechnology revolution. The fact that we can now make inorganic materials, as well as inorganic-organic composite materials, by processes such as layer-by-layer deposition, chemical vapor deposition, and laser ablation, means that the material we make is tailored by the process, just as a biochemical reaction is tailored by the available enzymes and reagents. One does not generally have to worry that we as organisms are metastable with respect to carbon dioxide and water. So, the richness of materials we can make depends on having control at the molecular level of the process that makes those materials.

A number of accidents, or perhaps fundamentals, of nature make this possible. The first is that in the solid state, many different structures are in fact very close to each other in energy, sometimes within the available thermal energy. A good example is zeolites with their framework structures. They are nanomaterials in the sense that they have immensely high surface areas of hundreds to thousands of square meters per gram. Those surfaces are primarily internal surfaces, which are structurally controlled. That topology, which is created by controlled synthesis, often using organic structure-directing agents, provides materials that, for example, are used for the cracking of petroleum or the synthesis of fine chemicals. So, we have the challenge on the one hand of making zeolites cheaply for these mass applications and on the other hand of making small amounts of very specialized materials, that is, designer zeolites

for designer chemicals. This is nanoscale science because the energetics at the interface of these zeolitic materials and the molecules within them, which either guides their synthesis or guides the reactivity of the molecules, enables a new set of technologies. The ability to cleverly design and constitute materials is the modern equivalent of a Maxwell demon—a creature that can select molecules at will. We tell molecules where to go and how to self-assemble. This is very critical to the nano revolution.

Nanomaterials beg an exact definition. A nanomaterial is something that has a nanoscale dimension. Scientists who have worked with colloid chemistry and surface science for 60 years say, "What's new about that? This is all just hype." I think what is new, from a fundamental point of view, is the realization that the basic questions of structure, of energetics, of properties, are common whether we are talking about a semiconductor, a carbon nanotube, a superconductor, a mineral, or an air-pollution particle. We might define a nanomaterial most broadly as one that has dimensions larger than that of a molecular cluster but smaller than that of a bulk material, but more importantly has an interesting property that is different from either. So, in a sense, if it quacks like a nanomaterial, it is a nanomaterial. If we have quantum confinement, a change in band structure, and a change in absorption frequency, we are dealing with phenomena on the nanoscale. If we have a suppressed melting point, we are dealing with nanoscale phenomena, and we seek to harness those phenomena for the application in question. It is no different from harnessing phenomena at the macroscopic scale, except that we now have an added richness.

From the point of view of earth science, which is one of the hats I wear, nature has been practicing nanotechnology probably since the beginning of the universe. Within condensation from the solar nebula, the initial particles that were formed were probably not well-crystallized, huge, single crystals. They were likely little, poorly crystalline, dust-grain nanoparticles that eventually grew, nucleated, condensed, came under pressure, and started the evolution of planets.

The surface chemistry of a planet such as Earth involves nanoscale processes. The weathering of rocks is corrosion at the nanoscale. The geochemical cycle then turns these weathered rocks into soil, into dust particles, and into sediments. Eventually, the sediments coalesce again and become rocks. That cycle involves primarily the reaction of particles at the nanoscale. If one

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thinks of soil science and agriculture, a soil is a most complex nanomaterial: mixed organic, inorganic, and biological materials of different sizes. Certainly, much of the transportation of nutrients, pollutants, organics, and heavy metals occurs at the nanoscale, that is, takes place on or around small particles. So, as earth environmental scientists, we are very interested in coated nanoparticles such as iron oxide nuclei with a bunch of harmful organics around them. The question is, will this go downriver until it gets into my water supply?

As atmospheric scientists, we are interested in nanoparticles. The nucleation of clouds is a nanoscale phenomenon: ice droplets, sulfuric acid droplets, cloud seeding. Thus, nucleation science is really nanoscale science. Any initial solid-state or condensed-phase reaction starts somewhere, and a few atoms do something. In that sense, the start of an earthquake, which may affect hundreds of kilometers, occurs somewhere with the breaking of a few chemical bonds. The origin of life and biochemical reactions have probably been mediated by mineral surfaces and, very likely, by mineral surfaces of small grains. Organisms even now, of course, contain iron oxide particles. Magnetotactic bacteria may use such particles to assist in vertical and north-south orientation. Birds may use them in navigation and homing. Mammalian brains, including ours, also contain some magnetic nanoparticles. Are they leftovers from evolutionary history, or part of functioning biological systems? The transport of nutrients such as iron, as well as the transport of heavy-metal pollutants such as cadmium and lead, often involves nanoparticles. Bacteria that do not depend on oxygen to provide energy sometimes obtain their energy from the consumption of variable oxidation-state nanomaterials such as iron oxides, manganese oxides, or uranium oxides. The phase transformations occurring in processes deep within a planet are often associated with a decrease in grain size, and the superplasticity associated with this phase transformation may be critical to earthquakes. The fundamental physical, magnetic, electrical, electronic, and chemical properties of nanomaterials need to be studied and characterized in order to understand their possible role in geologic processes.

Before leaving those fundamentals, let us address the interplay of theory and experiment. Many of the models that we have of the behavior of nanomaterials and interfaces are macroscopic models. The electrical double layer of structure near an oxide-water interface is essentially a macroscopic continuum model. Models of dielectric constants of ceramics, in which

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the structure of the ceramic may be heterogeneous on the scale of a nanometer, are continuum models. What do these bulk descriptions mean and, in particular, what do they mean when the particle or the material deviates from the behavior of its macroscopic counterpart—that is, when it shows true nanoscale behavior? To what extent are the bulk macroscopic mean-field theories applicable when the order we are observing is that of a few unit cells of the material? If such models are not applicable, what is? Certainly *ab initio* quantum calculations are applicable, but even with our most powerful computers doing these on a scale accurate enough for complex nanomaterials containing many different kinds of atoms, including heavy atoms, such computations are still a formidable task. So we simplify calculations by the tricks of systematics, semiempirical potentials, and so forth, and very often, then, we obtain an answer.

We still have a problem. On the one hand, we have a macroscopic description that does not accurately portray what happens on the atomic scale. On the other hand, we have a quantum description where the final numerical answer is the end in itself—but if the power goes off on our computer, we are not left with something that our brain can take and then extrapolate. So the real question is whether there exist systematics of chemistry at the nanoscale, of chemistry in less than a full three-dimensional array, that will give us the same sort of systematic predictions as Pauling's rules or concepts of ionicity or bond valence give us in a semiempirical but "graspable by the human mind" way for macroscopic materials. It is those sorts of systematics that interest me the most in my own research.

Many, many different structural states are easily accessible energetically. If they were not all close to each other, we would not be able to access them and maintain them. The very richness of our planet, of our chemistry, of our nanomaterials, and of ourselves depends on having this complex energy landscape, to use a physical chemist's formulation of it, in which many different states are possible. So, instead of having two forms of carbon, we have 20 different nanoscale forms of carbon; instead of having three or four silica phases, we have 30 or 40 metastable—but only

slightly metastable—silica zeolites. It is that richness we are exploiting.

Education

The second part of my talk deals with education, particularly graduate and postdoctoral education in the United States. What does one need to succeed in this field? What cultural patterns determine our careers? Nanoscience and nanotechnology are just part of our changing world, and I do not think "nano" can be blamed or praised for all of these changes. What we certainly still need in graduate education is the fundamentals. I decry people who call themselves chemists and physicists, and who sort of skate on the surface of science, without really having grasped the fundamentals. While there are more papers being written and published, there are more bad papers. I think we are having great difficulty sorting the wheat from the chaff simply because there is so much of it. So we need to teach our students the fundamentals and encourage them in critical thinking. We certainly need to train them in communication skills. Given that we have a global work force and that many of our students in the United States come with English as a second language, we need to be very, very concerned about language skills, both to communicate the science to the students and to have the students function well. We need to be equally concerned about the poor communication skills of our native-born. We also need to be concerned with communication between disciplines. We cannot be interdisciplinary, deep, and creative if we do not have a home discipline. On the other hand, we have to understand how to communicate with one another: how to overcome the barriers of jargon and to work in teams. Certainly, industrial teams are an example of successful collaboration. They are often made up of people trained in different fields but working together to solve one problem. However, even in university research, the tendency toward collaborative work—and toward the funding of collaborative work—gives us valuable experience.

Alas, the extreme is to have essentially all collaborations and nothing at the center of our own program, and that finally becomes a weakness. It becomes a tree with a rotten core, which cannot stand for long. That is a real danger. At universities, we think hard about how to broaden education and yet give students experience and knowledge that is deep in at least one discipline. For example, to understand the fate and transport of nanoparticles in the atmosphere, one needs to understand

their chemical origins, their aerodynamic properties, the meteorology of their environment, their chemical transformations, their adhesion and coalescence, and their interaction with living organisms. Each of these is a field in itself. How do we educate a student who wishes to work on atmospheric nanoparticles? Such training is not easy because it requires more, not less. To be interdisciplinary, we have to know more than one discipline in depth and a number of them at least by acquaintance. How do we do this? That is a big challenge to all of us.

### Societal Issues

The third issue that I would like to address is a broader societal issue, and it is to some extent nothing more and nothing less than the issue of good and evil in the world. Any science and any technology can be used for good or for evil. If we could simply separate those, we would be happy, but they are inseparable. If we look at where our science is now, many inventions that help people have come as a result of earlier investment in technologies that kill people. The military investment in electronics in the period from the Second World War (1940s) to the 1980s set the stage for the present-day richness of consumer electronics, medical diagnostics, and computer technology. Many capabilities that are terrible come hand-in-hand with those that are wonderful. Nanotechnology is not a new dilemma, but the acceleration of technology that nanotechnology makes possible certainly brings this dilemma to the fore. Let me give a small example, and perhaps even a harmless example, yet it illustrates the point.

I have dogs. Currently, it is routine to microchip pet dogs for a small fee. A company will sell a microchip that we or our veterinarian can inject through a needle under the skin of the animal. The chip has an electronically readable code num-

ber in it. If the dog gets lost and is picked up by the pound or a veterinarian, the animal can be traced and returned to the owner because the name and address are listed. This is a wonderful thing.

Now comes the next question: Is it a good idea to microchip human beings? For example, someone might have a medical condition and wear a bracelet or tag for it that might get separated from the person. If that person has a microchip instead that says, for example, I am a diabetic, personnel in an emergency room can immediately react accordingly. On the other hand, issues of privacy come in, and one can imagine the Big Brother sort of society where one can track the whereabouts of everybody or of a particular person. We can keep improving tracking procedures and the amount of information that is carried, and where does it stop?

These societal issues that come from what technology can do will always be with us. I do not blame nanotechnology any more than I blame the invention of fire. We will continue with our inventions, but we have to think about their consequences.

I would like to close with one issue that I find very disturbing. This thought is partly why I chose not to use PowerPoint or even overheads for my presentation. The problem is not that the medium is the message, but that the medium cheapens the message. We live in a barrage of sound bites, of glib and brief oversimplified messages. These messages focus, often poignantly, on one point, one image, one symptom, and not on its underlying complex causes. A good example is the latchkey child, the child who comes home after school when nobody is home. One sees an image of a child coming home to an empty house, an affluent high-tech house in a contemporary setting. The image suggests that somehow modern technology is responsible for the child's neglect. But the latchkey child is

a latchkey child whether the key is the old-fashioned one that Benjamin Franklin used on his kite, or a magnetic keycard with a nanophase iron oxide stripe on it, or some sort of biological recognition system that lets the child into the house. The change in technology is superficial. The child and the social problems remain. By emphasizing the technology, we have neither identified nor resolved the underlying social issues. We have to address them in a manner that is much deeper and more holistic than a 60-second analysis on our local TV station of the social effects of technological change.

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