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Understanding Nanotechnology

A BRIDGE TO THE FUTURE

Professor Deborah G. Sauder
Georgia Gwinnett College

Understanding Nanotechnology: A Bridge to the Future

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Georgia Gwinnett College



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Understanding Nanotechnology:

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Professor Deborah G. Sauder



Executive Editor

Donna F. Carnahan

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Producer - Ian McCulloch

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Editor - James Gallagher

Design - Edward White

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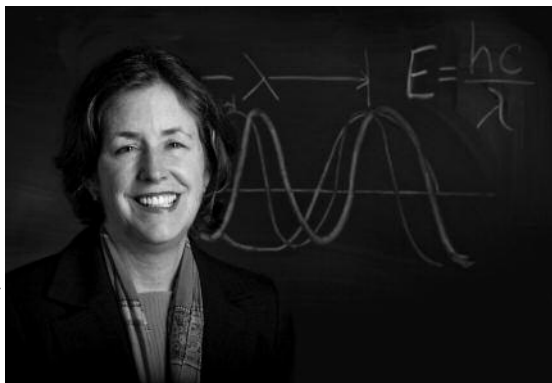
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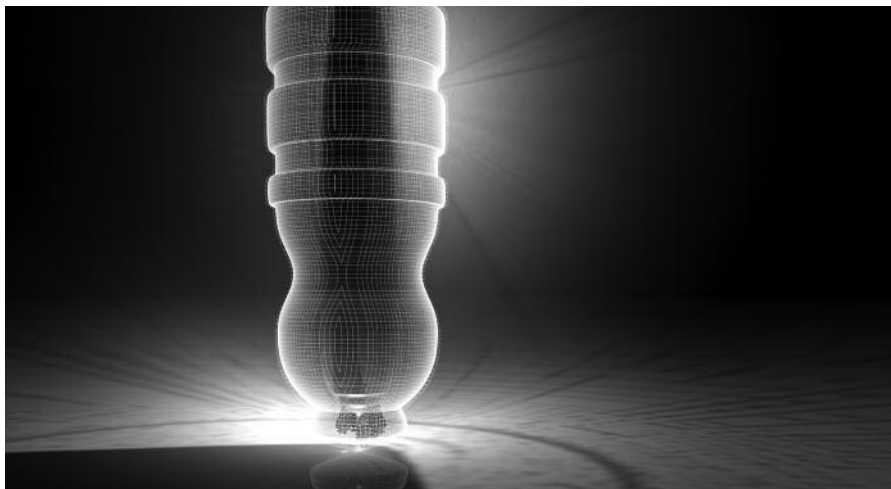
About Your Professor

Deborah G. Sauder

Deborah G. Sauder is an associate professor of chemistry at Georgia Gwinnett College in Lawrenceville, Georgia. She completed her Ph.D. in physical chemistry at Johns Hopkins University in 1991, followed by two years as a National Research Council postdoctoral research associate in the Molecular Physics Division at the National Institute of Standards and Technology in Gaithersburg, Maryland. She was soon after appointed to the faculty at Hood College in Frederick, Maryland.

Professor Sauder became involved in pedagogical reform efforts in the mid-1990s. She was an active participant in the Middle Atlantic Discovery Chemistry Project (MADCP), where she developed strategies to improve general chemistry student understanding of bond strength and of basic thermodynamics. As an outgrowth of these efforts, and under the leadership of Dr. Sharon Smith, emeritus professor of chemistry at Hood, she coauthored (with Smith, Kathryn Henry, and Karen Borgsmiller) Hood's "Experience Chemistry!" curriculum currently available from Pearson Custom Publishing. The curriculum was designed to promote conceptual understanding of basic chemistry in a diverse student body. It employs an integrated lab-lecture format and extensive use of hands-on activities. She was named a Project Kaleidoscope (Association of American Colleges and Universities) "Faculty for the Twenty-first Century" in 1997. Sauder was a founding member of the Physical Chemistry On-line (PCOL) consortium. The seven founding faculty members of PCOL shared the Gustav Ohaus Award for Innovation in College Science Teaching from the National Association of Science Teachers in 1999.

Dr. Sauder joined the Georgia Gwinnett College faculty in 2006. She is active in several professional organizations and most recently served as chair of the Georgia section of the American Chemical Society and as 2010 cochair of the Atlanta regional Project Kaleidoscope group.



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Introduction

Nanotechnology is a field where science fiction seems to predict science fact. Since the 1950s, an enormous number of technical and scientific innovations have been motivated by overcoming barriers to space exploration or analyzing data collected from manned and unmanned space exploration. Today, nanotechnologists envision a future in which space elevators built of carbon nanotubes move freight economically and ecologically to and from space to support a wide variety of manufacturing, exploration, and scientific goals.

On Earth, physicians dream of a magic bullet that would cure cancer, defeat sickle cell anemia, and stop Alzheimer's in its tracks. Efficient use of solar energy promises a solution to the ecological and economic problems faced by utilization of today's carbon-based fuels.

While addressing these challenges seems to require completely different skill sets, there is one thing they have in common. Solutions to them all are being imagined, researched, and tested by nanoscientists. Solving these problems may not be within the grasp of today's technologies, but continuing improvement in our sophistication in dealing with structures at the nanoscale makes many scientists optimistic that solutions are forthcoming in the not-too-distant future.

Lecture 1

Introduction and Overview

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 1: "Introducing Nano."

The truly fantastic science discussed in this course is not science fiction, but science fact. These scientific theories and laws have all been formulated by scientists carefully observing physical reality under highly controlled conditions, systematically testing hypotheses, and continually revising their models and theories.

This course begins with an introduction to the metric system. In most of the world, this would not be required, because in most of the world the metric system is the common system of weights and measures. But despite forty years of government-authorized effort, the metric system is still not familiar to most people in the United States.

Nanotechnology is extraordinary in that it is a branch of science that was predicted, with uncanny accuracy, by a scientist, Richard Feynman, thirty years before it was first realized. Lecture 3 features a discussion of Feynman's 1959 talk "There's Plenty of Room at the Bottom," which laid out the development of nanotechnology.

Lecture 4 is a discussion of "why size matters." This will introduce some physical consequences of small size. Those who have read *Gulliver's Travels* know that author Jonathan Swift sends his title character to the lands of the Lilliputians and the Brobdingnag and investigates the consequences of a "normal sized" being living in communities where the local scale is either one-twelfth or twelve times the size of the main character. The advantages or challenges Gulliver faces in Lilliput and Brobdingnag do not begin to approach the advantages and challenges of dealing with nanoscale systems—but at least Lilliput motivates us to begin thinking in the correct direction.

Lecture 5 examines the building blocks of nanodevices: atoms and molecules. One promising attribute of nanotechnology is that it deals with structures that are Lilliputian or Brobdingnagian in scale compared to proteins

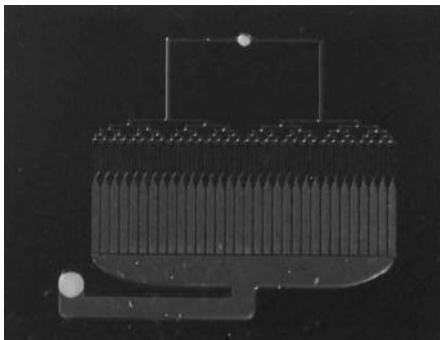


Image of a microscale singlet oxygen generator (microSOG). This is a gas-to-liquid separator assembled at the nanoscale and used in compact, efficient high-power lasers.

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and other important biomolecules. That is, nanoscale devices can interact in a direct way with amino acids, proteins, and other important biostructures, and they therefore offer new opportunities for synthesizing devices that can be designed to interact in specific ways with the molecules of life.

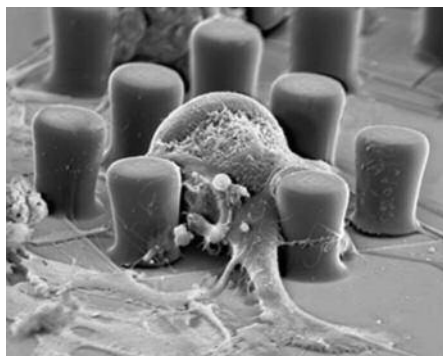
Lecture 6 is a brief introduction to some of the fundamental physics important in nanoscale devices. The lecture defines kinetic and potential energy and the first and second laws of thermodynamics. Then it considers Newton's laws of motion, the basics of optics, and current understanding of light and its interactions with matter. The lecture also examines Coulomb's law, which describes the interactions between two charged particles, and Ohm's law, which describes the motion of charge as current through electrical devices and circuits.

Lecture 7 describes the technologies that allow us to "see" nanoscale devices and describe their structures and motions. These very high-tech instruments depend on everything from the oddest of physically real phenomena—tunneling—to some easy-to-understand uses of light and lasers.

Lecture 8 considers a variety of strategies for building nanostructures and nanoscale devices. The techniques are usually considered to divide into two different approaches, top down and bottom up. In top-down formation of nanostructures, one begins with a slab of material and carves away the unwanted components. In bottom-up assembly, one starts with individual atomic components and assembles them in a step-by-step fashion, the way a hobbyist builds a scale replica of a seafaring ship or a race car. Of course, working at the nanoscale presents some unusual challenges.

Lecture 9 looks at the promise of nanoscale sensors and introduces the concept of sensors and transduction of signals, talks about the benefits of a wide variety of sensors, and applies the fundamental concepts of chemistry and physics to explain why and how sensors work.

In Lecture 10, the focus is on the use of nanotechnology in medicine. Some of the most spectacular concepts in nanotechnology are in the realm of molecular motors. Human beings depend on a treasure trove of all types of molecular motors. Some help maintain ion balance in our cells, some move resources from where they are to where they are needed, and others allow our



A nanotechnology team headed by Professor Maria Strømme at the Ångström Laboratory in Uppsala, Sweden, explores the possibilities of using vacant pores in semiporous particles of silica where a pharmaceutical ingredient can be placed for direct transfer to specified cells in the body and better protect the medicine from being broken down when deposited into a moist environment.

muscles to move us through space in precisely controlled ways. Through her creation of these wonderful little machines, Mother Nature has inspired many nanoscientists to devise equally elegant nano-machines that will eventually solve a multitude of health-related problems.

Lecture 11 considers the consequences of nanoscale electronic devices on the speed, capacity, and ubiquitousness of computers. The lecture also identifies social concerns that essayists are raising about the consequences of the miniaturization of computer components and devices. The lecture talks about Moore's law and Moore's second law, examines today's state-of-the-art in integrated circuits, and revisits the lesson on physics to illustrate some of the problems that will need to be overcome to allow truly nanoscale computing to occur.

Lecture 12 addresses the application of fundamental science to predict and explain the use of nanotechnology in energy production and transmission. Among the topics is how nanotechnology promises to vastly improve the efficiency of photovoltaic devices, how nanotechnology is already leading to the development of energy-scavenging devices to provide local energy sources for small devices, and how nanoscale manufacturing is improving light emitting diode performance.

Lecture 13 imagines the possibility of nano "smart materials" and the ways in which they could improve our lives. A smart material is a material that alters its structure and function in response to an environmental stimulus. Smart materials that you might be familiar with are the lenses in sunglasses that turn dark when exposed to sunlight. Similar smart materials might soon be used in car windows. They could be darkened when you park in the summer to prevent the incredible buildup of heat with which most of us are familiar. Or they could be used in building windows to allow a maximum amount of light in on cold days and darken to reduce solar radiational heating on hot days.

Finally, Lecture 14 considers brave new world consequences postulated by some ethicists to result from the maturation of nanotechnology. Given the ubiquitous nature of unintended consequences, many scientists are participating in wide-ranging discussions of both the intended positive and possible negative consequences that may result from the rapid development of nanotechnology. Of course, most scientists are confident that technological progress benefits mankind—and nanotechnologists are no different.

FOR GREATER UNDERSTANDING

Questions

1. Why is Richard Feynman important in the history of nanotechnology?
2. To what technologies do Moore's laws apply?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

Booker, Richard D., and Earl Boysen. *Nanotechnology for Dummies*. Indianapolis, IN: Wiley Publishing, Inc., 2005.

Scientific American, eds. *Understanding Nanotechnology*. New York: Warner Books, Inc., 2002.

Websites of Interest

1. *Bloomberg Businessweek* magazine provides an article entitled "The Business of Nanotech," from February 14, 2005. — http://www.businessweek.com/magazine/content/05_07/b3920001_mz001.htm
2. The *National Nanotechnology Initiative* website provides a multiagency framework to ensure United States leadership in nanotechnology. — <http://www.nano.gov>
3. The *Nano Science and Technology Institute* promotes the integration of small technologies through education, technology, and business development. — <http://www.nsti.org>
4. *Nanotechnology Now* provides information about nanotechnology to business, government, academic, and public communities with a current collection of reference material. — <http://www.nanotech-now.com>

Lecture 2

The Metric System

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 1: "Introducing Nano."

The metric system is the system of units used most widely in the world and most extensively in science. The metric system, or System International, has seven fundamental units. In this course, we will be most concerned with the unit of mass, the kilogram (kg); the unit of distance, the meter (m); and the unit of volume, the liter (L). By some miracle, the base unit of time, the second (s), is the same in both the English and metric systems.

In other situations you might need to consider the ampere (unit of current), the candela (unit of luminosity), or the mole (quantity of matter), but they are not a concern here. Every metric unit used by today's scientists, technologists, manufacturers, and entrepreneurs is derived by combining only these seven base units.

The metric system has an advantage over the English system of units in that it is a decimal system. So if you are using the metric system, you could convert from meters to decimeters by multiplying by 10, and from decimeters to centimeters by multiplying by 10. In contrast, the English system requires you to remember that 1 mile is 5,280 ft. and multiply a distance measured in miles by 5,280 to convert it to feet. To convert a measurement in feet to inches, you need to remember that 1 foot is 12 inches and multiply the number of feet by 12 to get the number of inches. If you want to measure something smaller than an inch, you can subdivide the inch into eighths, sixteenths, or thirty-secondths. Everyone needs a calculator to do those conversions.

In science, as in life, people usually choose the units in which they measure something to match the scale of the item they are measuring. For instance, while you might report the diameter of a penny in inches, you would probably not report the diameter of the Earth in inches—although you certainly could. Choosing appropriate measuring devices is both a practical matter reflecting how the measurement is actually made and a question of optimizing resolution or accuracy. The smaller the unit used, the more precise the measurement is expected to be.

It is easy to talk about both very large and very small items using the metric system. The decimal nature of the metric system makes it easy to scale the base units to be appropriate for any measurement and makes it easy to convert between units once a measurement is made. In the metric system, standard prefixes are used to scale the base units. Think of a

large number—the distance from our Sun to the nearest star. That distance is about 40 petameters. That's 40 followed by 15 zeroes, when the distance is measured in meters, to the nearest star. The metric prefix “peta” means $\times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10$ meters. Scientists say the distance to the nearest star is 40 petameters, or 40×10^{15} m. Or they can abbreviate “peta” by writing a capital “P” in front of the “m.” Therefore, 40 petameters, 40×10^{15} m, and 14 Pm all mean the same thing.

The notation 40×10^{15} m is in “scientific notation.” In scientific notation, scientists report the numbers they measure in regular decimal format, but report the order of magnitude or scale of the measurement by multiplying by the appropriate number of factors of ten. The multiplier 10^{15} means that to get the distance from the Sun to the nearest star in units of meters, you need to multiply 40 (the measured value) times 10 fifteen times.

The kilogram, the standard unit of mass, is equal to 1,000 g. The prefix kilo means $\times 1,000$ or times 10 times 10 times 10 ($\times 10 \times 10 \times 10$) or 1×10^3 . The kilometer is 1,000 m, or 1×10^3 m. The abbreviation for kilo is a lower case k, so kilogram is written kg, kilometer is km, kiloliter is kL. The prefix kilo brings the metric system into the realm of units we encounter every day. A kilosecond is 16 minutes and 40 seconds. A kilogram is about the mass of a 1 L bottle of water. A kilometer is about the distance you would walk if you went four blocks in Manhattan. The metric prefix kilo describes the scale of items we deal with every day.

Although there are prefixes in the metric system that mean $\times 100$ and $\times 10$, they are not in wide use today. This discussion started with units that are 10^{15} times larger than the base units of the metric system. The base units are essentially “human scaled.” You are between 1 and 2 m tall, you probably weigh between 25 and 125 kg, and you can easily carry a liter of water around with you and drink it during the day. Space, the solar system, the planet, and Bill Gates's fortune require large units to measure their dimensions. But we can convert any of the larger units discussed so far to describe larger-scale items to the smaller units with which we are familiar by multiplying by a sufficient number of 10s.

In the metric system, if the size of the unit we employ to make a measurement is decreased by a factor of 10, simply move the decimal on the number one place to the right. If the size of the unit is decreased by a factor of 100, move the decimal on the number two places to the right. However, in the discussions so far, you may note that scales have been changed by factors of 1,000. Using the smaller unit of “m” instead of kilometers means the decimal is moved three places to the right. For instance, I live about 25 miles (or 40 km) from my office. So I drive 40 km each way. If I report that distance in meters, a unit 1,000 times smaller than km, the distance would be 40,000 m. I moved the decimal on 40 three places to the right to convert from units of km to units of m.

On the other hand, if I want to buy a carpet for my hallway, I would look for a carpet that would fit in a space about 1 m wide and 3 m long. If I reported these dimensions in km instead of m, I would move the decimal to the left because the unit is getting bigger. My hallway has dimensions of about 0.001 km wide and 0.003 km long. In employing the larger unit of km rather than m, I have moved the decimal three places to the left.

You will note that we have yet to encounter the prefix “nano.” And “nano” is the most important prefix in this course. Nano is among the prefixes that describe units smaller than the standard metric unit. Unlike the prefixes that apply to larger measurement units, the prefixes for 1/10 and 1/100 are in as common use as the prefix for 1/1,000. The prefix deci, abbreviated d, means 1/10. The prefix centi, abbreviated c, means 1/100. Milli (abbreviated m) means 1/1,000. Note that the symbol m does double duty in the metric system—it can stand for the unit of distance, m, or the multiplier 1/1,000. You need to infer the meaning from the context.

When talking about metric system units smaller than mg, ms, or mm, things start going down by factors of 1,000, just like they went up by factors of 1,000 when we were considering units larger than the base units. One one millionth is called micro. A micrometer, 1/1,000,000 of a meter, is 1/1,000 of a millimeter. The abbreviation for micro is the Greek lower case letter “mu” (μ).

Table 1.1: Metric Prefixes

metric prefix	abbreviation	decimal multiplier	scientific notation
peta	P	1,000,000,000,000,000	$1.0 \times 10^{+15}$
tera	T	1,000,000,000,000	$1.0 \times 10^{+12}$
giga	G	1,000,000,000	$1.0 \times 10^{+9}$
mega	M	1,000,000	$1.0 \times 10^{+6}$
kilo	k	1,000	$1.0 \times 10^{+3}$
base unit		1	1.0×10^0
deci	d	0.1	1.0×10^{-1}
centi	c	0.01	1.0×10^{-2}
milli	m	0.001	1.0×10^{-3}
micro	μ	0.000001	1.0×10^{-6}
nano	n	0.000000001	1.0×10^{-9}
pico	p	0.000000000001	1.0×10^{-12}
femto	f	0.000000000000001	1.0×10^{-15}

Things that are at the “micro” scale are approaching the limit of our ability to see or feel them. A human hair is about 200 μm in thickness. A dollar bill is about 100 μm thick. Ragweed pollen is about 20 μm in diameter and the bacteria *E coli* are tube shaped and about 2 μm long. Both pollen and bacteria can be seen under appropriate magnification. A grain of sand has a mass of about 1.0 mg, but weighing one grain takes a pretty sophisticated balance.

It is worth taking a moment at this point to get a sense of the difference in scale between a meter and a millimeter and between a millimeter and a micrometer. A meter is about a yard. A millimeter is about the thickness of a penny. A micrometer is half the length of an *E coli* bacterium. Each is three orders of magnitude or a factor of 1,000 smaller than the previous item. To get to the nanoscale, we need to go down another *three* orders of magnitude, or a factor of 1,000, from here.

The prefix “nano” means 1 billionth, 1×10^{-9} or 1/1,000,000,000 and is abbreviated n. A nanometer is one billionth of a meter—or 1 billion nm is one meter. A nanogram is 1 billionth of a gram. A nanoliter is 1 billionth of a liter. That means that a ng is to a gram (which is less than half a penny) as 149 m (~163 yards, or one and two-thirds of a football field) is to the distance between Earth and the Sun. You can’t see or feel a nanogram of anything—in fact, you usually can’t even smell or taste it.

To get a sense of how small an nm is, note that the average atom is about 0.1 nm in diameter. Because it is the right size to describe atoms, the distance 0.1 nm gets a special, trivial name—it is called an angstrom (Å).

The standard metric prefix smaller than nano is pico, 1×10^{-12} . An atom with a diameter of 1 angstrom or 0.1 nm has a diameter of 100 picometers, 100 pm. Although you might assume that chemists have no need of units smaller than the size of an atom, there is one smaller unit used with some frequency—the next smaller metric prefix is femto, 1×10^{-15} . An atomic

Table 1.2: Base Units of the Metric System

metric unit	abbreviation	measures
kilogram	kg	mass
meter	m	distance or length
liter	L	volume
second	s	time
ampere	amp	electrical current
candela	cd	luminosity of a light source
mole	mol	quantity of matter

nucleus, the feature that contains all the positive charge and the vast majority of the mass of an atom, is between 2 and 15 femtometers in diameter. The fastest lasers can investigate phenomena that occur in 10 to 100 femtoseconds, a timescale on which electrons can rearrange. This is the timescale on which nascent chemical reactions are investigated.

This lecture discussed distances that differ by thirty orders of magnitude, from 10^{+15} m to 10^{-15} m. For most scientists, this covers the distance dimensions with which they are concerned. But there are a variety of other very large and very small numbers that chemists use routinely to talk about the chemicals all around us. Some of the most common are the mole, the atomic mass unit, and the electron charge.

Because atoms and molecules are so small, it takes a lot of them to provide an amount we can detect with our senses. Just as we usually buy eggs or donuts by the dozen—another name for a collection of twelve items, chemists give a special name to a collection of a standard number of atoms or molecules—the number is just really big. The special name is a “mole.” Think of it as related to “molecule,” not to the small furry animal with poor eyesight. A mole of anything is 6.022×10^{23} items. If you measure a volume of 18 mL of water, about equivalent to a heaping tablespoon, the water sample will contain 6.022×10^{23} molecules of water: one mole of water. The sample will have a mass of 18 g, which is about seven pennies. The mass and volume of a mole of atoms or molecules depends on the size of the atoms or molecules. Just like a dozen eggs are not the same weight or size as a dozen donuts, a mole of water is not the same mass or volume as a mole of copper or a mole of nitrogen.

The forces between atoms that allow them to form molecules, to hold together as liquids or solids, or to engage in chemical reactions are all due to the electrical properties of the electrons and protons of which they are composed. The charge on a single electron or proton sounds small, -1.6×10^{-19} coulomb for the electron and $+1.6 \times 10^{-19}$ coulomb for the proton, but remember that the size of electrons and protons is small, too—so the attraction between oppositely charged protons and electrons is big enough to give obsidian, steel, and concrete their strength, and their rearrangements are responsible for the heat from a fire and produce the energy required to move your car down the road.

FOR GREATER UNDERSTANDING

Questions

1. Describe the relative scales of English and metric units by choosing the qualifier in parentheses that completes each sentence correctly:
 - a) A gram is (about the same as; substantially less than; substantially more than) a pound.
 - b) A liter is (about the same as; substantially less than; substantially more than) a quart.
 - c) A meter is (about the same as; substantially less than; substantially more than) a yard.
2. Why have scientists universally adopted the metric system as their standard units of measurement?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

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Scientific American, eds. *Understanding Nanotechnology*. New York: Warner Books, Inc., 2002.

Articles of Interest

Zewail, Ahmed H. "Filming the Invisible in 4D: New Microscopy Makes Movies of Nanoscale Objects in Action." *Scientific American*. August 16, 2010.

Websites of Interest

1. The *Powers of Ten* website provides an update of a classic educational film originally made by IBM that shows the relative size of things in the universe and the effect of adding another zero. —
<http://www.powersof10.com/film>
2. A *View from the Back of the Envelope* website by software engineer Mitchell Charity of Vendian Systems features information and exercises designed to help understand scientific notation. —
<http://www.vendian.org/envelope>

Lecture 3

“There’s Plenty of Room at the Bottom”

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner’s *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 4: “Interlude Two: Tools of the Nanosciences.”

In December 1959, Richard Feynman delivered the lecture “There’s Plenty of Room at the Bottom”^{*} at an American Physical Society meeting at the California Institute of Technology. In this talk, Feynman laid out a challenge to chemists and physicists to figure out how to control things at an atomic scale. And as you’ll hear, Feynman did an uncanny job of predicting the development of nanotechnology many years before anybody had conceived of being able to do anything at the nano scale:

I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle. This field is not quite the same as the others in that it will not tell us much of fundamental physics (in the sense of, “What are the strange particles?”) but it is more like solid-state physics in the sense that it might tell us much of great interest about the strange phenomena that occur in complex situations. Furthermore, a point that is most important is that it would have an enormous number of technical applications.

What I want to talk about is the problem of manipulating and controlling things on a small scale.

As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord’s Prayer on the head of a pin. But that’s nothing; that’s the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below.



Richard P. Feynman
(1918–1988)

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^{*} Feynman, Richard P. “There’s Plenty of Room at the Bottom: An Invitation to Enter a New Field of Physics.” A lecture given to the annual meeting of the American Physical Society on December 29, 1959, at the California Institute of Technology in Pasadena, California. Used by permission of the *Engineering & Science* magazine. Ed. Douglas L. Smith. California Institute of Technology, Pasadena, CA.

Feynman's challenge to the academic and research communities at the time was to start thinking seriously about controlling things on a nanoscale.

The head of a pin is a sixteenth of an inch across. If you magnify it by 25,000 diameters, the area of the head of the pin is then equal to the area of all the pages of the *Encyclopaedia Britannica*.

Therefore, all it is necessary to do is to reduce in size all the writing in the *Encyclopaedia* by 25,000 times. Is that possible? The resolving power of the eye is about $1/120$ of an inch, that is, roughly the diameter of one of the little dots on the fine half-tone reproductions in the *Encyclopaedia*. This, when you demagnify it by 25,000 times, is still 80 angstroms in diameter—32 atoms across, in an ordinary metal. In other words, one of those dots still would contain in its area 1,000 atoms. So, each dot can easily be adjusted in size as required by the photoengraving, and there is no question that there is enough room on the head of a pin to put all of the *Encyclopaedia Britannica*.

Furthermore, it can be read if it is so written. Let's imagine that it is written in raised letters of metal; that is, where the black is in the *Encyclopaedia*, we have raised letters of metal that are actually $1/25,000$ of their ordinary size. How would we read it?

If we had something written in such a way, we could read it using techniques in common use today. (They will undoubtedly find a better way when we do actually have it written, but to make my point conservatively I shall just take techniques we know today.) We would press the metal into a plastic material and make a mold of it, then peel the plastic off very carefully, evaporate silica into the plastic to get a very thin film, then shadow it by evaporating gold at an angle against the silica so that all the little letters will appear clearly, dissolve the plastic away from the silica film, and then look through it with an electron microscope!

Feynman says there is no problem doing this. They just needed to figure out how to make the electron microscope do what they wanted it to do. But the bigger question than reading it was how to write it.

We have no standard technique to do this now. But let me argue that it is not as difficult as it first appears to be. We can reverse the lenses of the electron microscope in order to demagnify as well as magnify. A source of ions, sent through the microscope lenses in reverse, could be focused to a very small spot. We could write with that spot like we write in a TV cathode ray oscilloscope, by going across in lines, and having an adjustment which determines the amount of material which is going to be deposited as we scan in lines.

What Feynman is describing here is a process called rastering. When we write with a pen we write one letter at a time. But if you were to print you would run a raster across a paper, writing one line at a time. You would

move down the paper, moving down one step every time. Imagine a typewriter in which each key, instead of writing a full letter, writes only a small fraction of a letter. Feynman is imagining a way of controlling the amount of ink that winds up on a paper, but not writing a full letter at one time. This method of writing one line at a time would be pretty slow.

There will be more rapid methods. We could first make, perhaps by some photo process, a screen which has holes in it in the form of the letters. Then we would strike an arc behind the holes and draw metallic ions through the holes; then we could again use our system of lenses and make a small image in the form of ions, which would deposit the metal on the pin.

In this case, Feynman is describing using a stencil, essentially, except that this time we draw metal atoms through the stencil, not ink or paint.

A simpler way might be this (though I am not sure it would work): We take light and, through an optical microscope running backwards, we focus it onto a very small photoelectric screen. Then electrons come away from the screen where the light is shining. These electrons are focused down in size by the electron microscope lenses to impinge directly upon the surface of the metal. Will such a beam etch away the metal if it is run long enough? I don't know. If it doesn't work for a metal surface, it must be possible to find some surface with which to coat the original pin so that, where the electrons bombard, a change is made which we could recognize later.

These techniques would allow us to put the *Encyclopaedia Britannica* on the head of a pin. But, says Feynman, let's consider all the books currently published in the world (which Feynman hypothesized to be 24 million).

It would take, of course, the area of about a million pinheads because, instead of there being just the 24 volumes of the *Encyclopaedia*, there are 24 million volumes. The million pinheads can be put in a square of a thousand pins on a side, or an area of about 3 square yards. That is to say, the silica replica with the paper-thin backing of plastic, with which we have made the copies, with all this information, is on an area of approximately the size of 35 pages of the *Encyclopaedia*. . . . All of the information which all of mankind has ever recorded in books can be carried around in a pamphlet in your hand.

This is a stunning consequence of the scale of nanotechnology. Hence the title of Feynman's talk, "There's Plenty of Room at the Bottom." What he has demonstrated by his discussion of putting all the books in the world on one storage space at the nanoscale is that there is plenty of room to do interesting things in nanoscale technology.

Feynman next turned to the technology that was available in 1960 to look at nanoscale devices.

The electron microscope is not quite good enough; with the greatest care and effort, it can only resolve about 10 angstroms. I would like to try and impress upon you, while I am talking about all of these things on a small scale, the importance of improving the electron microscope by a hundred times. It is not impossible; it is not against the laws of diffraction of the electron. The wavelength of the electron in such a microscope is only $1/20$ of an angstrom. So it should be possible to see the individual atoms.

And he asked rhetorically, "What good would it be to see individual atoms distinctly?" Well, let's think about some applications.

What is the sequence of bases in the DNA? What happens when you have a mutation? How is the base order in the DNA connected to the order of amino acids in the protein? What is the structure of the RNA; is it single-chain or double-chain, and how is it related in its order of bases to the DNA? What is the organization of the microsomes? How are proteins synthesized? Where does the RNA go? How does it sit? Where do the proteins sit? Where do the amino acids go in? In photosynthesis, where is the chlorophyll; how is it arranged; where are the carotenoids involved in this thing? What is the system of the conversion of light into chemical energy?

It is very easy to answer many of these fundamental biological questions; you just look at the thing! You will see the order of bases in the chain; you will see the structure of the microsome. Unfortunately, the present microscope sees at a scale which is just a bit too crude. Make the microscope one hundred times more powerful, and many problems of biology would be made very much easier.

Since Feynman's talk, many of these questions in biology have been answered and the resolution for looking at biological systems has improved dramatically. Sufficiently that we can in fact tell the order of bases in DNA; we know where the RNA goes; we know how the proteins sit; and we know how the chlorophyll works in photosynthesis. Feynman's point, however, is that if you answer biological questions by looking at biological things, then you should be able to answer chemical and physical questions by looking at chemical and physical things. The challenge is that chemical and physical things are a lot smaller than biologically interesting ones.

Feynman turned his interest to computers. In 1960, nobody had a desktop or laptop or cell phone that allowed them to access the World Wide Web. In fact, the Web didn't exist. So the short history since 1960 has led to a tremendous increase in the sophistication and use of computer technology.

I don't know how to do this on a small scale in a practical way, but I do know that computing machines are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements—and by little, I mean little. For instance, the wires should

be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across. Everybody who has analyzed the logical theory of computers has come to the conclusion that the possibilities of computers are very interesting—if they could be made to be more complicated by several orders of magnitude. If they had millions of times as many elements, they could make judgments. They would have time to calculate what is the best way to make the calculation that they are about to make. They could select the method of analysis which, from their experience, is better than the one that we would give to them. And, in many other ways, they would have new qualitative features.

Feynman asks the question, How can we make a device tremendously smaller than the devices we have now?

One possibility we might consider, since we have talked about writing by putting atoms down in a certain arrangement, would be to evaporate the material, then evaporate the insulator next to it.

He's talking here about making computer devices.

Then, for the next layer, evaporate another position of a wire, another insulator, and so on. So, you simply evaporate until you have a block of stuff which has the elements—coils and condensers, transistors and so on—of exceedingly fine dimensions.

But I would like to discuss, just for amusement, that there are other possibilities. Why can't we manufacture these small computers somewhat like we manufacture the big ones? Why can't we drill holes, cut things, solder things, stamp things out, mold different shapes all at an infinitesimal level? What are the limitations as to how small a thing has to be before you can no longer mold it? How many times when you are working on something frustratingly tiny, like your wife's wrist watch, have you said to yourself, "If I could only train an ant to do this!" What I would like to suggest is the possibility of training an ant to train a mite to do this. What are the possibilities of small but movable machines? They may or may not be useful, but they surely would be fun to make.

Consider an automobile. We need an accuracy of $4/10,000$ of an inch to have all the pieces fit together and work properly. If I want to make the automobile a million times smaller than it really is, $4/10,000$ of an inch isn't accurate enough to make the pieces fit together anymore. If I reduce the size of the car by a million, I need to reduce my tolerance for errors in my parts by a million as well. So Feynman pulls the following information from fundamental physics.

It is interesting to consider what the problems are in such small machines. Firstly, with parts stressed to the same degree, the forces

go as the area you are reducing, so that things like weight and inertia are of relatively no importance. The strength of material, in other words, is very much greater in proportion. The stresses and expansion of the flywheel from centrifugal force, for example, would be the same proportion only if the rotational speed is increased in the same proportion as we decrease the size. On the other hand, the metals that we use have a grain structure, and this would be very annoying at small scale because the material is not homogeneous. Plastics and glass and things of this amorphous nature are very much more homogeneous, and so we would have to make our machines out of such materials.

The electrical system on the car would have to shrink, too. And magnetic properties change on a very small scale and are different from large-scale magnetic properties.

The electrical equipment won't simply be scaled down; it has to be redesigned. But I can see no reason why it can't be redesigned to work again.

Feynman addresses the question of lubrication in very small objects. He says that "actually we may not have to lubricate at all!" Because our car is so small, the heat that is generated, that feature that requires lubrication in our macroscale cars, is very much smaller too. That heat can escape very quickly from small devices.

Feynman looks at the surgical arena and suggests an interesting possibility: Wouldn't it be interesting in surgery if you could swallow your surgeon? Your mechanical surgeon could run around inside your blood vessels and go to your heart and fix the valve that it encounters. "Other small machines might be permanently incorporated in the body to assist some inadequately-functioning organ." But how do we make such tiny mechanisms?

One way is to manufacture very small tools and use a traditional method of producing machines. But this becomes complicated quickly. Building nanoscale wrenches, screwdrivers, hammers, lathes, and machines is a nontrivial problem. So it might make better sense to think differently about how to structure these tiny machines.

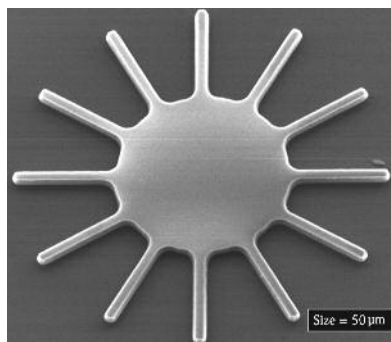
Feynman points out that as we go down in size, there are a number of interesting problems. Things do not just scale down in proportion. There is the problem that materials stick together by molecular or van der Waals attractions. After you made a part, and you unscrewed the nut from the bolt, it isn't going to fall down. It isn't heavy enough for gravity to pull on it. What would happen if instead of building nanoscale devices the same way we build macroscale devices, we could come at it from the other side. What if we could build nanoscale devices one atom at a time?

Feynman says he can't exactly see how this could happen, but it does seem like we should be able to control the arrangement of things on a small scale and get materials with unique properties, and unique machines out of the process.

When we get to the very, very small world, say a circuit of several atoms only, we have new behaviors that provide new opportunities for design. Atoms on a very small scale behave completely differently than macroscopic samples of atoms. This is because small scale requires atoms to satisfy the laws of quantum mechanics. We can use not just circuits, but quantized energy levels, or the interactions of quantized spins. And if we get small enough, all devices that are mass produced will be exactly, absolutely perfect copies of one another. It is impossible for us at the macroscale to build two machines that are exactly the same. There are always minor variations. But if you build a machine that is only 100 atoms high, you've got to get it exactly correct, or it just won't be the same machine. So on the exactly correct replica we get the benefit of having instruments or machines that always behave in exactly the same way.

There's no physical principle that we are going to violate by trying to control things atom by atom. But in the time of Feynman, it hadn't been done, because we didn't have the tools we needed to move atoms around and make them do what we want them to. Today, at the beginning of the twenty-first century, we are starting to develop those tools and we are starting to learn how to use them to build nanoscale machines and devices.

In a utopian perspective, lots of scientists would tell you that nanotechnology, because of its efficient use of energy and raw materials, is truly the greenest of strategies for moving forward into the twenty-first century.



"MEMS" Devices to Filter and Amplify Electronic Signals

Researchers are developing a new class of tiny mechanical devices containing vibrating, hair-thin structures that could be used to filter electronic signals in cell phones and for other more exotic applications. The work is done inside a vacuum chamber sitting on top of a special vibration-absorbing platform critical to making the precise measurements. A tiny prototype (above) is roughly comparable in size to a grain of sand. The device is an example of a microelectromechanical system (MEMS), which contains tiny moving parts.

FOR GREATER UNDERSTANDING

Questions

1. According to Feynman's estimate, how large a space is required to store all the information in all the books written (as of 1960) if each bit of information is represented by 100 atoms?
2. What does Feynman identify as the principal difficulty in making nanoscale devices?
3. What substantial improvement is possible when you are building machines that are only 100 atoms high, when compared to even miniature machines from 1960?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

Feynman, Richard P. *The Pleasure of Finding Things Out: The Best Short Works of Richard P. Feynman*. New York: Helix Books/Perseus Publishing, 2005.

Websites of Interest

1. The California Institute of Technology library provides the text (and a downloadable pdf of Caltech's *Engineering & Science* magazine's printed article from 1960) of Richard P. Feynman's lecture "There's Plenty of Room at the Bottom." —
<http://calteches.library.caltech.edu/47/2/1960Bottom.htm>
<http://calteches.library.caltech.edu/47/2/1960Bottom.pdf>
2. The *Engineering & Science* magazine website at Caltech features recent issues of its publication. — <http://EandS.caltech.edu>
3. The Foresight Institute (Palo Alto, CA) has awarded the annual Feynman Grand Prize for Major Advances in Molecular Nanotechnology since 1996 to encourage and accelerate the development of molecular nanotechnology. —
http://www.foresight.org/prize/feynman_distinctions.html

Lecture 4

Why Size Matters

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 2: "Size Matters."

Why is nanotechnology such a big deal? Isn't it just making smaller and smaller versions of things we already have? Investigating some of the factors that make nanoscale structures and devices fundamentally different from those typical-sized items with which we are familiar sheds light on just how different nanotechnology can be.

Properties of Materials

An important consideration is in the ratio between an object's surface area and its volume. For instance, this ratio controls the rate at which ice melts. Even when held at the same temperature, a snowball melts more quickly than a person-sized snowman, not just because the snowman is larger, but also because the snowball has a larger surface area compared to its volume.

The cube provides a familiar object to help investigate the ratio between surface area and volume. Every cube can be described by the length of its sides, the area of its surface, or its volume.

A die is a solid. It has a surface that is the boundary between the die and the surrounding space. Assume it measures 2 cm along each side. If we wanted to build a paper object enclosing the same volume as the die, we would need six paper squares, each one 2 cm on each side. The area of any square is its length times its width. Each of our squares has an area of $2\text{ cm} \times 2\text{ cm} = 4\text{ cm}^2$. Areas are reported in units of length squared. The units are multiplied times each other, just as the lengths are multiplied to get the area.



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We calculate the volume occupied by any cube by taking the width \times the depth \times the height. For our die, the volume is $2\text{ cm} \times 2\text{ cm} \times 2\text{ cm} = 8\text{ cm}^3$. The volume of a container is reported in length units *cubed*, because the volume determines the number of cubes 1 unit on each side that fit in the volume in which we are interested.

Even physical properties of objects can depend not just on what they are made of, but on their surface area or volume, or the ratio between the two. For the die, the volume is 8 cm^3 and the surface area is 24 cm^2 , so the ratio is 0.3 cm.

As the cube gets bigger, the ratio between its volume and surface area gets bigger, too. What does this mean in practical terms? It means, for example, that it takes a manufacturer less cardboard to make one big box to hold ten items than it does to make ten individual boxes, one for each item.

The fact that large objects have proportionally less surface area than small objects has consequences in biology and engineering, too. At the small end of the biological spectrum, the surface area to volume ratio in single-cell organisms is important. Nutrients and oxygen need to diffuse through the cell membrane and into the cells. Most cells are no longer than 1 μm in diameter because small cells enable nutrients and oxygen to diffuse into the cell quickly and allow waste to diffuse out of the cell quickly.

In engineering, the materials available to build a structure define limits on the size of the building that can be constructed. Single-family homes in the United States are typically built of wood over a masonry foundation. Look around any modern city today, and you will find buildings that exceed 167 m in height. Taller buildings require steel framing and the tallest result from a combination of steel and reinforced concrete. As the height and volume of a building increase, the need for structural strength to support the occupants and to provide stability in high wind conditions (which depend in part on the volume-to-surface-area ratio for the building) require different structural materials.

But all these examples, even the single-cell organisms, are huge in comparison to nanoscale objects. Nevertheless, the properties of nanoscale objects are also dependent on volume-to-surface-area ratios. For example, probably the historically oldest application of nanotechnology is in the use of very finely ground gold metal as the source of pigmentation in both stained glass and some pottery. We think of gold as gold in color, but medieval window makers knew that gold, ground into a sufficiently small dust, and added to molten glass, produced spectacular colors, including red, orange, green, and purple. Today, we know that these colors depend on the size, and, specifically, the volume-to-surface-area ratio, of the nanoscale gold particles.

The dramatic property changes observed for nanoscale structures are not entirely due to volume-to-surface-area ratios, though. The nanoscale is so small that the relevant rules of physics change as well.

We are familiar with the macroscale, which we will define as everything larger than 1 micrometer in dimension. We will define nanoscale as things that are 1 to 100 nm in dimension. In our macroscale universe, the behavior of objects is governed by Newtonian, or classical, mechanics. The fundamental physical principles governing the motion of objects are summarized in Newton's three laws.

Everything that we directly experience, from the moon and asteroids to rockets to cars to bullets to a ball bearing 1 micrometer in diameter, follow Newton's laws of motion, first articulated in the late 1600s:

1. An object in motion remains in constant motion unless a force acts on it.
2. A change in motion depends on the magnitude of the force applied and the mass of the object.
3. For every action, there is an equal and opposite reaction.

Newton's second law is mathematically expressed as $F = ma$; force = mass \times acceleration. It allows us to calculate trajectories and describe motion whether we are NASA scientists trying to determine how to get a lander on Mars or a CSI agent trying to determine the trajectory from the location of a body, the shell, and the bullet fragment lodged in the wall. In classical mechanics, we know that an object goes faster when we push on it, that it is attracted to the Earth by the force of gravity, and that air and tire friction are the bane of high-gas-mileage vehicles.

Historically, Newton's first law was informed by the law of inertia advanced by Galileo, in direct contrast to Aristotle's assertion that objects sought their own levels. Aristotle thought that things remained fixed until a force acted on them. But he ignored one very important complication—friction. Galileo and Newton correctly understood that friction was acting on almost all objects in motion. And Newton described that an object in motion in a frictionless environment would continue in motion in that environment until a force, including the force of friction, acted upon it.

Physicists spend a lot of time trying to imagine or to create frictionless environments. In the twentieth century, European and Japanese engineers took advantage of the friction reduction that magnetic fields provide and built “MagLev” trains. These trains float in a magnetic field and use most of their fuel to move forward, not to overcome friction between the wheels and the tracks.

How can we comprehend the change from the classical world we inhabit to the quantum world of the nanoscale that permeates our universe? One traditional entry is to think in a very detailed way about how we detect our surroundings. Specifically, consider sight. Sight is dependent on photons of light interacting with objects and being delivered to our eyes, where we detect them and our brains translate this signal detection into macroscopic items. But there are obvious limits to our vision.

We believe in air, not because we can actually see it, but because we can see its aggregated effects. Why is it that you can see the leaves and limbs of a tree move in the wind, but you can't see the air that *is* the wind? Air is a gas, while leaves and trees are solids. But being a solid or a gas is not sufficient distinction. When there is a fire, you often see billowing clouds of smoke that sure look gaseous. If you are inside looking at a tree outside, you are probably looking through glass, which certainly appears to be a solid. What is the property that determines whether or not we can see

something? To answer that, you need to recall the classical picture that light behaves like a wave.

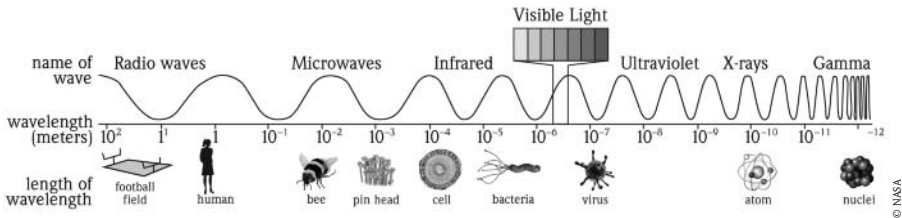
If I asked you to draw a wave, you would probably draw a wiggly line with identifiable peaks and valleys. In science, we use the trigonometric sine (or cosine) function to describe perfect waves. Both your drawing and the perfect sine function show stationary waves. The stationary wave is characterized by its amplitude, A , or how high the wave is and its wavelength, λ , the distance between one wave peak and the next. To represent light coming to our eye, we need to imagine the wave moving through space. The sine function wave traveling through space is characterized by a third parameter—its frequency, or how many waves pass a given point in a second.

If you have ever thrown stones into a pond, you have studied waves. The waves start at the point where the drip or the stone hits the surface of the water. It propagates outward at a speed we can monitor. You can see the peaks and valleys and estimate the amplitude and wavelength of the waves. You can focus on one point in space and count the frequency of waves passing that point. And if your water container is big enough, you can see friction degrade the wave, so that it disappears from your sight if you get far enough from the source of the wave.



Our visual sense responds to particular waves—those associated with visible light. Visible light is just a small portion of the electromagnetic spectrum. The electromagnetic spectrum is divided into sections based on the wavelength of the light. In general, chemists and physicists identify the parts of the electromagnetic spectrum according to the ways radiation of different wavelengths interacts with matter. A typical division of light is into gamma rays, X-rays, ultraviolet light, visible light, infrared light, microwave radiation, and radio waves, reported from shortest to longest wavelengths.

Figure 4.1: Types of Waves and Wavelengths



One interesting thing about light waves is that the wavelength of the wave times its frequency equals its speed of propagation. According to Einstein, the speed of light is always constant, 2.998×10^8 m/s. Our definition of electromagnetic radiation is now radiation that travels at 2.998×10^8 m/s in a vacuum. Therefore, we can calculate the frequency of any electromagnetic radiation from its wavelength. The frequencies of the electromagnetic spectrum range from $\sim 3 \times 10^4$ to 10^{24} cycles/s or $\sim 3 \times 10^4$ to 10^{24} Hertz.

Also according to Einstein, light, which we classically consider to be a wave, can also behave like a particle. Specifically, light carries and transfers energy as if the energy were packaged in little bundles in amounts proportional to the light's frequency. The proportionality constant is called Planck's constant, named after the scientist who first derived it. Planck's constant is a very small number. One particle, or photon, of light carries an incredibly small amount of energy on a macroscopic scale.

Imagine then that billions of waves with wavelengths of about 500 nm hit a car, bounce off it, and strike your eye. You see the car. What does the car do? Even a very small car is more than a meter high and more than a meter wide and more than a meter deep. And it has a mass of one or two thousand kilograms. So the car really doesn't respond in any detectable way to the light hitting it.

But when the same photons that hit the car bounce into your eye, they cause a substantial effect. The individual photons of light are absorbed by the individual light-sensing molecules in your eye. The absorption promotes a detectable change in the molecules in your retina. This molecular change begins a cascade of chemical and electrical events that allow your brain to register that you "see" the car. The molecular effect happens in part because photons of visible light and molecules in your retina are the correct scale to interact with each other. Molecules that absorb (or emit) a photon can undergo both energetic and structural changes because they are of the correct scale and contain electrons at appropriate energies for individual photons to make a difference. The changes are not necessarily those you would envision from the analogy of shrinking the car. In fact, we need an entirely new mechanics, quantum mechanics, to fully describe and interpret changes on the single photon–single molecule scale.

FOR GREATER UNDERSTANDING

Questions

1. Who is primarily responsible for the modern understanding of the laws of physics that govern the motion of macroscale objects?
2. What is the name of the mechanics needed to describe the interactions between electromagnetic radiation and nanoscale objects?
3. Name the regions of the electromagnetic spectrum from longest wavelength to shortest wavelength.
4. Identify one of the earliest applications of nanotechnology.

Suggested Reading

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Articles of Interest

Buffat, Phillipe H., and Borel, J.P. "Size Effect on the Melting Temperature of Gold Particles." *Physical Review A*. Vol. 13, no. 6. Pp. 2287–2298. College Park, MD: The American Physical Society, 1976.

Websites of Interest

The *Computer Support Group* website provides an online surface-area calculator for different shapes, including cones, cubes, cylinders, rectangular prisms, and spheres. — <http://www.csgnetwork.com/surfareacalc.html>

Lecture 5

The Chemical Building Blocks of Nano

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 3: "Interlude One—The Fundamental Science Behind Nanotechnology."

Atoms are named for the Greek *atomos*, the smallest piece of matter into which Greek philosophers believed objects could be cut. Today, the atomic theory is accepted as the fundamental basis of chemistry. The 118 atoms on the periodic table compose all the matter in the universe. If you can touch it, feel it, taste it, or smell it, it is made of atoms.

Atoms can combine in a number of ways. They form molecules, ionic solids, metals, semiconductors, and polymers, depending on how they collectively allocate their electrons.

Today's periodic table began to take form in the 1860s. Chemists of the time distinguished metals from non-metals. Metals were elements that were shiny, malleable, and ductile. They were confident that Antoine Lavoisier's 1789 law of conservation of mass was correct. Lavoisier was able to show experimentally that the total mass of a system does not change when a chemical reaction occurs. They also knew of Joseph Proust's law of definite proportions, which said that a compound always contains the same elements in the same mass ratios, independent of the source of the compound or the quantity examined.

In the early 1800s, John Dalton proposed the law of multiple proportions. Dalton's law said if two elements can combine to form more than one compound, the ratio of the masses of the second element that combine with the first will yield small whole number ratios. Consider carbon and oxygen, which form two distinct compounds. In one, the mass of oxygen that combines with 6 g of carbon for one compound is 8 g; in the other it is 16 g. The ratio of the masses of oxygen is 1:2, a ratio of small whole numbers. Dalton explained his law by hypothesizing that chemical elements are composed of indivisible atoms. Furthermore, all the atoms of one element are identically the same, and atoms are not created, destroyed, or altered by chemical reactions, simply rearranged in different combinations.

Amedeo Avogadro's experiments with gases led him to propose that equal volumes of any two gases, at equal temperature and pressure, contain equal numbers of molecules. Avogadro recast the question of mass ratios by studying the volume ratios in which gaseous elements reacted. He observed that two volumes of hydrogen react with one volume of oxygen to form two volumes of water vapor. From this data, Avogadro concluded that the oxygen

split in half, and half combined with each volume of hydrogen. The elemental oxygen was diatomic—two atoms of oxygen bonded together to form the gaseous compound that supported combustion and respiration in humans, and which was produced by plants. Because of this improvement and better experimental results, Avogadro produced more accurate estimates of the mass ratios of oxygen and other elements to hydrogen and articulated the distinction between molecules and atoms.

Avogadro also made one of the first efforts to count the number of molecules in his samples. As a result, he gave his name to the very large number that chemists use to count the number of atoms or molecules in a sample. Avogadro's number, 6.022×10^{23} , gives the number of atoms in a sample that have a mass in grams equivalent to the mass of an individual atom in atomic mass units (amu). So whereas one H_2 molecule has a mass of about 2 amu, Avogadro's number of hydrogen molecules has a mass of about 2 grams. Just as 12 are a dozen, 20 is a score, and 500 is a ream, chemists say that Avogadro's number of atoms or molecules is a mole of atoms or molecules.

Despite the contributions of many, most chemists credit Dalton with the establishment of today's atomic theory of matter:

1. Matter is made of atoms, which are neither created nor destroyed.
2. All atoms of a given element have the same mass and the same properties, and are different in mass and properties from all other atoms.
3. Two or more different kinds of atoms combine in small whole-number ratios to form compounds.
4. Chemical reactions are caused by a *rearrangement* of atoms.

As the field of chemistry grew, more and more elements were isolated. Their masses and combining ratios were determined. Chemists began to note some patterns in the behavior of the elements.

In 1864 and 1865, English chemist John Newlands ordered the known elements according to their atomic weights, and he noted that the physical and chemical properties of the elements appeared to replicate every eight elements, like octaves in music. Building on this foundation, chemists Dmitri Mendeleev (in 1869) and Julius Lothar Meyer (in 1870) independently published periodic tables. They both listed the elements in order by atomic weight and began a new cycle when the characteristics of the elements began to repeat. Their tables also had octaves.

Mendeleev's table was more successful for two reasons. He left spaces in his table when he felt an element was missing and he used the trends in his periodic table to predict the properties of those missing elements. He also switched the order of some pairs of elements, putting the heavier element before the lighter when their properties seemed to demand it.

Mendeleev's table was accepted in the scientific community, but no one could explain why the elements demonstrated a periodic repetition of their properties. The explanation began to be revealed in 1897. And it required nothing less than a revolution in the understanding of physical reality.

The mechanical inventions that powered the industrial revolution also allowed scientists unprecedented levels of control over their samples. They could subject materials to higher and lower temperatures than ever before. They could create vacuums and high-pressure environments. More reliable measuring devices were developed, allowing both temperature and pressure to be recorded to new levels of precision.

A second scientific revolution began when J.J. Thomson modified a tube designed by Sir William Crookes (1832–1919) to examine the particle nature of *cathode rays*. Crookes' tube used a long glass cylinder divided into several sections from which the air was removed, leaving only vacuum behind. At one end, a small amount of gas was added to the tube in the presence of two wires that connected to an external battery, which supplied a high voltage. The battery's cathode was set on the long axis of the tube, and the anode some distance away. Under correct conditions, rays were emitted from the cathode. These rays could be focused through a tiny slit in the anode and accelerated by a secondary anode, also with a slit, at a higher voltage than the first. Some distance down the tube, a set of plates connected to other external batteries and oriented perpendicularly to the first set generated another electric field. The end of the tube was coated with a phosphor, which produced visible light when the cathode beam hit it.

Thomson's experiments with Crookes' tubes showed that the cathode rays, which were known to be deflected by magnetic fields, could also be deflected by electric fields. He concluded that cathode rays were not light but were rather composed of very lightweight particles—he called them *corpuscles*—that were negatively charged. Thomson thought that these corpuscles emerged from the gas molecules near the cathode. He correctly deduced that atoms *were* divisible and proposed that these small negatively charged corpuscles were building blocks of atoms. Because he knew that bulk materials were composed of neutral atoms and molecules, Thomson also suggested that his negative corpuscles were distributed in a uniform sea of positive charge. This model is called the “plum pudding” model, as the electrons were embedded in the sea of positive charge like plums in a plum pudding.

In 1909, Ernest Rutherford, who had been a student of Thomson's, correctly interpreted experiments done by Hans Geiger (of the Geiger tube) and Ernest Marsden and overturned Rutherford's plum pudding model.

Geiger and Marsden used a source of alpha particles, which were known to have a mass approximately four times that of a hydrogen atom and also known to carry a positive charge that balanced that of two of Thomson's

Table 5.1:
THE PERIODIC TABLE OF ELEMENTS

[illegible]

Sources: Illustration by Scott E. Van Bramer, Widener University, Chester, PA (1990); 1905 IUPAC masses and Approved Names from the International Union of Pure and Applied Chemistry (<http://www.chem.qmul.ac.uk/iupac/atw/>); masses for 107–111 from *Chemical & Engineering News* (C&EN), March 13, 1995, p. 35; 112 from <http://www.gsi.de/z112e.html>; 114 from C&EN July 19, 1990; 116 and 118 from Berkeley Lab (<http://www.lbl.gov/Science-Articles/Archive/elements/116-118.html>).

corpuscles. They shot the alpha particles at a piece of gold foil. Their assumption was that the positive sea in the gold foil would allow the alpha particles to pass through with only slight deflections. Eventually, Geiger and Marsden made the gold foil target so thin the alpha particles were able to get through. While most of the alpha particles went directly through the foil, or were only slightly deflected, a few of the alpha particles bounced almost straight back. Rutherford is famously quoted as having remarked that these results were “about as credible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you.”

The large deflections observed by Geiger and Marsden were explained by Rutherford by reconceiving the structure of matter. No longer did it appear that electrons were embedded in a sea of positive charge.

Rutherford explained the results by confining the positive charges and most of the mass of an atom to a very small fraction of its total volume, which he assumed was at the center of the atom. The lightweight, negative electrons occupied a cloud of space around the positive charge. Only this high concentration of mass and positive charge could cause an electric field strong enough to deflect the alpha particle trajectories to such a large degree.

Today, chemists categorize the ways that atoms combine to form the infinite number of materials around us by considering how the atoms hold together and according to the physical and chemical properties of the materials. For the purposes of this course, materials will be categorized into covalent compounds, polymers, ionic compounds, metals, and semiconductors.

Covalent Compounds

Covalent molecules are discrete collections of atoms bound together by sharing electrons. Superficially, the goal appears to be to allow each atom to hold an octet of electrons. The periodic behavior described by the periodic table implies an “octet rule,” which states that atoms can achieve a minimum energy configuration by acquiring eight electrons in their outermost,

Table 5.2:
Symbols and Names of
Common Elements

Ag	Silver	He	Helium
Al	Aluminum	K	Potassium
Ar	Argon	Li	Lithium
Au	Gold	Mg	Magnesium
B	Boron	Mn	Manganese
Be	Beryllium	N	Nitrogen
Br	Bromine	Na	Sodium
C	Carbon	Ne	Neon
Ca	Calcium	Ni	Nickel
Cl	Chlorine	O	Oxygen
Co	Cobalt	P	Phosphorus
Cr	Chromium	Pb	Lead
Cu	Copper	S	Sulfur
F	Fluorine	Si	Silicon
Fe	Iron	Ti	Titanium
H	Hydrogen	Zn	Zinc

or valence, orbital. Covalent compounds are generally composed of non-metallic elements, all sharing their electrons so that they obtain octets.

Molecules exist as independent entities that are only weakly connected to each other; therefore, they can be observed as solids, liquids, or gases under typical conditions. When phase changes occur, they are accompanied by separation of molecules from one another as the temperature increases, but not usually by any change in the molecular composition or structure.

Covalent compounds have electrons localized near and between the nuclei of their atoms and are therefore observed to be poor electrical conductors. The molecule's mass is determined by the sum of the masses of its constituent atoms.

Extensive networks of covalent bonds are found in particularly hard, inert, and high-melting-temperature materials, like diamond. Diamond is essentially pure carbon. In diamond, each carbon atom is covalently bonded to four other atoms in a pyramidal arrangement called a tetrahedron. The four bonds mean that each carbon atom is surrounded by an octet of electrons. The directional nature of covalent bonds means that the structure is very rigid and very strong at the atomic level.

Polymers

Very high mass covalent compounds are generally composed of large numbers of simpler covalent units repeated many times in a regular or semi-regular pattern. The largest covalent compounds are called polymers. Common polymers include nylon in your stockings or carpet, cellulose in wood, and the fats in olive and other oils. All of these polymers are constructed of carbon, hydrogen, nitrogen, and oxygen atoms in specific arrangements. Some polymers behave like uncooked spaghetti noodles; their long chains of covalent bonds are rigid in space. Others behave more like cooked noodles; they are very flexible and sticky. The variety of behaviors contributes to the vast array of uses to which synthetic polymers are put in modern society.

Ionic Compounds

Ionic compounds, like the salt on your table, are fundamentally different from covalent compounds. They are held together by the electrical forces between opposite charges. Ionic compounds generally form between metals and non-metals, or metal ions and molecular ions. Ionic compounds form when one element is willing to give electrons to or accept electrons from another element. In every case, the atoms try to give away or accept enough electrons to actually get an octet of electrons, as octets provide the most stable or lowest energy configuration for most elements.

In addition to the salt on your kitchen table, ionic compounds form a lot of the rocks of the earth's surface, and a variety of more exotic compounds. Ionic compounds are almost exclusively found as crystalline solids at normal temperatures. Those that dissolve in water form aqueous solutions that

conduct electricity. Those that can be melted without decomposing conduct electricity in the molten state.

Metals

The ancients knew about the properties of metals and discovered a lot of practical chemistry in their efforts to turn base metals, like lead, into valuable metals like gold. Metals are different from covalent and ionic compounds. They are shiny, and they conduct heat and electricity. Most are solids at room temperature (the exception is mercury). The solids are malleable, able to be hammered or formed into shapes without breaking, and ductile, able to be drawn into wires. Today's model of metals returns, in a sense, to Thomson's plum pudding model. The picture is that the metallic nuclei arrange themselves in a regular three-dimensional pattern but contribute their valence electrons to a sea of electrons that surround the entire nuclear structure. Metals are socialistic in their arrangements—they throw all the available electrons in one pot and share amongst all. Because the electrons are fluid, they can easily rearrange themselves under the influence of an applied electric field, or to chase the nuclei as they are rearranged under the force of a hammer blow.

Semiconductors

The last category of materials is the most important in the electronic revolution we are experiencing today. Semiconductors are solids that take on properties intermediate between those of covalent and metallic compounds. Silicon is a primary example. Pure silicon has a structure very similar to that of pure carbon, because it is immediately below it on the periodic table. But, because of its large number of electrons, and therefore larger size, it is easier to remove an electron from silicon than from carbon. This ease makes it possible to set some electrons in silicon free from the nuclei, allowing silicon to conduct electricity under specific conditions, or in the presence of specific atomic partners. This semiconducting property is the basis of our modern electronic revolution.

Metals, semiconductors, and ionic solids are all forms of matter where the traditional properties of bulk materials might be expected to change when samples are sliced and diced down to nanosize. The most obvious change is when metals are divided into nanoscale pieces—color and melting point have already been noted.

Small covalent molecules are in a sense nanoscale to begin with—lots of individual molecules are nanometers long or wide or high. But the observable properties of covalent compounds are determined not only by their size but also in the way individual molecules relate to each other in space. The physics of nanoscale systems turns out to be fundamentally different from the physics of human-scaled objects, as will be seen.

FOR GREATER UNDERSTANDING

Questions

1. What does Dalton's law of multiple proportions say? How does it support the atomic theory?
2. What do we call J.J. Thomson's corpuscles today?
3. What is an "octet"?
4. Do nitrogen and oxygen form ionic compounds, covalent compounds, or semiconductors?
5. Do sodium and chlorine form ionic compounds, covalent compounds, or semiconductors?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

Fine, Leonard W. *Chemistry*. Chapter XX. New York: Appleton-Century-Crofts, 1972.

Websites of Interest

1. The *American Chemical Society* website provides an interactive periodic table. — <http://acswebcontent.acs.org/games/pt.html>
2. The *Royal Society of Chemistry* website features a "Chemistry Timeline." — <http://www.rsc.org/chemsoc/timeline>
3. A *YouTube* video featuring the reaction of lithium and water. — <http://www.youtube.com/watch?v=n1VbwwZHskU>
4. A *YouTube* video featuring the reaction of chlorine and sodium. — <http://www.youtube.com/watch?v=Mx5JJWI2aaw>

Lecture 6

Some Essential Physics

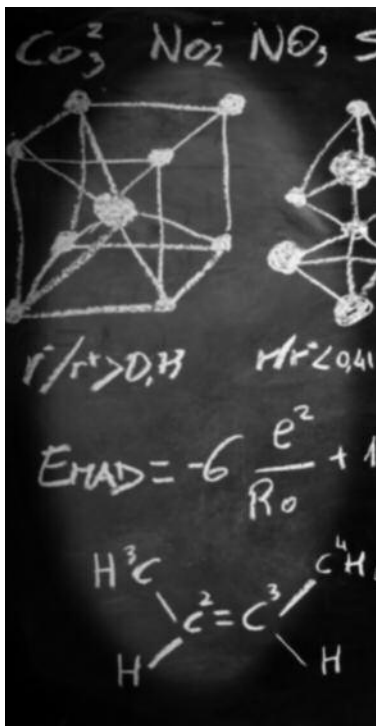
The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 3: "Interlude One—The Fundamental Science Behind Nanotechnology."

The law of conservation of energy says that the energy of the universe is constant. Energy is not created or destroyed, but it can be transformed.

Two of the most familiar types of energy are kinetic and potential. Kinetic energy is energy of motion. Potential energy is energy of position. Physicists calculate kinetic energy by taking the mass of an object times its velocity squared. Kinetic energy = $KE = \frac{1}{2}mv^2 = \frac{1}{2}mv^2$.

Potential energy comes in a variety of forms. Gravity is the force that acts between any two objects that have mass. Near the surface of the Earth, objects have gravitational potential energy determined by their mass and their height above the surface. Mathematically, $V = mgh$, where V is the potential energy, m is the mass of the object, h is the height of the object above the Earth, and g is the acceleration due to gravity, 9.8 m/s^2 . Note that the units on potential energy, $\text{kg}(\text{m/s}^2)\text{m}$ are the same as the units on kinetic energy, $\text{kg}(\text{m/s})^2$. In the metric system, 1 kg moving at a velocity of 1 m/s has a kinetic energy of $1 \text{ kg m}^2/\text{s}^2$, or 1 joule. That same 1 kg mass has a potential energy of 1 J when it is 0.102 m above the surface of the Earth. Of course, if you lift a 1 kg mass up to 10.2 cm above the surface of the Earth, you need to hold it there. If you let go of it, it will fall to the Earth. It is attracted by the Earth's gravity and acted on by the gravitational force: $F(\text{gravity}) = -GMm/r^2$.

G is the universal gravitational constant, M is the mass of the Earth, m is the mass of the object near the Earth, and r is the radius of the Earth plus h , the height of the object above the surface of the Earth. The force tells you about how quickly the potential energy is changing when the object moves along the line connecting it to the center of the Earth.



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Another important kind of potential energy is electrostatic energy. Because electrons and protons carry opposite charges, they are attracted to each other by the electrostatic force, in just the same way that the 1 kg mass and the Earth are attracted by the gravitational force. The force between two charges is given by $F(\text{electrostatic}) = kq_1q_2/r^2$.

This is also called Coulomb's law. The constant k is called Coulomb's constant, q_1 is the charge on one object, and q_2 is the charge on the other object. The r gives the distance between the centers of the objects. You will recall the old saying "opposites attract." The saying is motivated by Coulomb's law. When there is a negative sign in Coulomb's law, it means the two charges are attracted to each other. Unlike gravity, which is always attractive, electrostatics can produce both attractive and repulsive forces. The attractive forces result when one charge is positive and one is negative. If the two charges are the same, either two electrons or two protons, the force is positive, or repulsive.

One of the problems with the "solar system" model of atomic structure is that classical electrodynamics predicts that the electrons should be attracted to their positive nuclei. Just like the mass falls to the earth when you let go of it, classical electrostatics predicts that electrons should fall into their nuclei. Falling demonstrates a fundamental property of physical systems—they prefer to be at minimum potential energy. This is true for systems where gravity is the most important force and for macroscopic systems where electrostatic interactions are most important. But it fails when considering very small things like electrons.

In molecules, atoms share electrons. Sometimes the electrons are uniformly distributed throughout the molecule, but sometimes they are not. The uniformity, or lack thereof, is determined both by the properties of the individual atomic components and their arrangement in three-dimensional space. The individual atomic property that is important is "electronegativity," a measure of the tendency an atom has to pull a bonding electron pair toward itself. In general, electronegativity increases across a row on the periodic table and decreases down a column.

When the distribution of electrons in a molecule is uniform, the molecule is *nonpolar*. When the charge distribution is not uniform, molecules are *polar*. Polar molecules contain regions where there is a higher than average concentration of electrons and regions that are deficient in electrons. Because of their non-uniform electron distributions, polar molecules appear to have a positive end and a negative end. The magnitude of the charge separation and the distance of the separation are described quantitatively as a dipole moment. Polar molecules do not have a net charge, but they do have a non-zero dipole moment.

A dipole moment can cause an orientation-dependent force between two molecules. For instance, the negative end of one HCl molecule is attracted

to the positive end of another HCl molecule, but it is repelled from the positive end.

Chemical systems are no different from other physical systems—they try to arrange themselves to get to minimum potential energy. Because the individual atoms and electrons are so light in mass, gravity is not very important in chemical systems. But because of the large numbers of atoms and even larger numbers of electrons in most chemical systems, they are described as having chemical potential energy—the aggregated electrical potential energy of all the atoms in the system. Chemical potential energy is ultimately electrical potential energy. But when systems contain lots of atoms, chemists tend to focus on the aggregate chemical energy, and not on the specific electrical energy between two of the many atoms. In chemical systems, the charge distribution is the most important factor contributing to the potential energy of the system.

If energy is conserved, how can one change the kinetic or potential energy of a system? Heat and work are also forms of energy, and they can be used to convert kinetic energy to potential energy, or vice versa.

People have an intuitive sense of what work is, but physicists have a specific definition: Work is moving a mass some distance d against an opposing force F : $W = -Fd$.

The Second Law of Thermodynamics

One statement of the second law of thermodynamics says the entropy of the universe is always increasing. Entropy is a scientifically formal name for disorder. The second law is commonly restated: the disorder of the universe is always increasing. This is less obviously useful than the first law.

When your car is running, the chemical energy in the gasoline is converted to kinetic energy of your car—and you. If you have a perfectly level commute to work, the chemical energy in the gasoline gets converted to the kinetic energy of you and your car. There is no change in the gravitational potential energy, so no work is done against the gravitational field. However, and this is part of Newton's breakthrough, if there is no friction, your car doesn't move. You just spin your wheels.

What's friction? Friction is the result of the attractive forces between two surfaces. The gravitational attraction between your car and the earth means that your tires push down on the molecules that make up the road. The molecules in the road push back on your tires with an equal and opposite force. Friction is reduced when your car is in motion because of the transient nature of the interaction between your tires and the molecules in the roadway. Friction is what allows your tires to push on the road and not just spin freely. As a consequence of friction your car moves forward when you provide fuel to your engine. Also as a consequence of friction, your car stops when you take your foot off the gas, whether or not you apply your brakes.

Friction is such a ubiquitous part of existence that for centuries man did not perceive it. In ancient Greece, Aristotle contended that the natural state of bodies was “at rest” because he knew that everything in motion tended to slow down in time and stop moving. He interpreted “rest” as the “natural state” of bodies, because he had not considered the role of friction. Newton revised Aristotle’s picture by asserting that *a body in motion stays in motion, unless acted on by an outside force*. Newton had figured out friction. Today, we know that Newton’s statement is accurate, and Aristotle’s is not.

Cars are not 100 percent efficient, which means that only some of the chemical potential energy released when you burn gasoline is converted to motion of your car. How does physics define efficiency? Perhaps the most useful definition for the car example is that efficiency, ϵ , is defined as $\epsilon = \text{work done}/\text{energy supplied}$.

Your car does work by moving you around, even on a perfectly level surface where its gravitational potential energy doesn’t change. Why aren’t cars 100 percent efficient? A physicist would blame it on the second law, which can be interpreted to mean that some of the energy supplied by burning gasoline in a car engine causes the car to move, but some of it is released as heat. Your engine and tires both get hot when your car is moving. The second law says that no matter how good your engineering ability, it will always be the case that some of the chemical energy in the gasoline is released as heat.

In nanoscale structures, electrostatic potential energy and kinetic energy are both important. And the second law is still in force. If we want to move electrons through a circuit to provide a current in an electrical device, we have to provide energy to move them from their minimum energy position. It is always true that the work done on (or by) the electron is less than the energy supplied. The difference shows up as heat.

Light

Until the early 1900s, the classical view of physics was that light and matter were different things. Light had no mass and was a wave. Matter had mass and behaved like a particle, which, according to Newton, traveled in straight lines at constant velocity until acted on by a force. But there was a problem with light. *All* other wave behavior was observed as causing fluctuations in matter. Water waves move water, sound waves move air. What did light waves move? Scientists hypothesized the existence of a material called an ether that fluctuated, transmitting light waves. But nobody could find the ether. Finally, in 1887, Albert Michelson and Edward Morley set out to test once and for all whether there was an ether. Their results indicated that there was no ether, and therefore light was different from other waves in that it did not appear to need a medium in which to propagate.

Meanwhile, at the end of the nineteenth century, other experiments started to break down the distinction between waves and particles. A blackbody is a theoretical object that absorbs 100 percent of the light that hits it. It does not reflect anything and appears perfectly black. In practice, no material has been found to absorb all incoming radiation, but carbon in its graphite form absorbs all but about 3 percent. Materials that are very good at absorbing light are also good at emitting it—if you can get them hot enough.

Blackbodies both emit and absorb every wavelength of light. Even before 1900, the wavelength at which a blackbody emits the most energy was observed to depend on its temperature. Standard blackbody radiation curves, showing the intensity of light emitted at each wavelength, were measured. The higher the temperature of the blackbody, the higher the frequency at which its highest emission intensity occurred.

Classical physics held that the atoms in a blackbody were bound together by chemical bonds that behaved like little springs. The atoms could vibrate around their rest positions, and as with all charges in motion, would thereby radiate energy. The motions were associated with natural or standing waves of the structure. More standing modes were associated with high-frequency motions; in fact, the number of modes increased as the square of the frequency. Increasing numbers of modes meant increasing intensity of emission.

Unfortunately, the picture of classical physics did not match the experimental observations, which showed that the radiator's emission intensity peaked at specific frequencies related to the temperature but fell off as the frequency of the radiation increased further. This discrepancy was dubbed the “ultraviolet catastrophe,” because it was in the high-frequency, ultraviolet part of the spectrum that the prediction differed from the experiment.

In 1924, German physicist Max Planck (1858–1947) asserted that the energy of oscillators in solids was not continuous but was quantized. This meant that in a blackbody, the frequencies of the oscillating electrons could have only certain values. Planck said that the energy of the oscillator was proportional to its frequency ($E = hf$), and today the proportionality constant h is called Planck's constant ($h = 6.626 \times 10^{-34}$ Js). Later application of Planck's model allowed scientists to correctly match theoretical curves of the intensity radiated by a blackbody at each frequency to the experimental data. The blackbody ultraviolet catastrophe was resolved by assuming that energy was not continuously distributed in a blackbody but was only allowed to occur at certain discrete, quantized energy levels. Quantum mechanics was born.

When Planck's idea was applied to electrons in atoms—they were asserted to have only specific quantized energies. These energies could be associated in hydrogen atoms, via Coulomb's law, with an average radial separation

between the nucleus and the electron. When the electron jumped from one allowed radial separation to another, the energy of the electron-nucleus system changed. The energies of photons in the emission spectra of the hydrogen atom correlated exactly with the energy gaps between different quantized energy levels of the electrons in the hydrogen atom.

Meanwhile, Albert Einstein was trying to resolve the discrepancies between theory and experiment in the photoelectric effect, which is observed when light shines on metals. Sometimes the light causes electrons to be ejected from the metal surface. Experiments show that not all light can cause electrons to be ejected from all metals. In a gross generalization, no matter how bright a red light you have, it will not produce a current from a metal. But even a very dim blue light will produce a current.

The problem was that these results can't be explained if light behaves like a wave. A wave's energy is associated with its amplitude—big waves have a lot of energy, small waves have very little. And if light is a wave, then the brightness of the light reflects its amplitude—the brighter the light, the bigger the wave, the more energy it has.

The results of the photoelectric effect, however, indicate that different colors of light have different amounts of energy, independent of their intensity. If all else is equal, blue light has more energy than red light, with yellow light somewhere in between. Einstein realized that the only way to explain the photoelectric effect was to say that instead of being a wave, as was generally accepted, light was delivering energy to metals in small packets of energy he called photons. The photons behaved like particles of light.

With light as photons, Einstein showed that red light can't dislodge electrons because its individual photons don't have enough energy—the impacts are just not large enough to shift the electrons. However, blue light can dislodge electrons because each individual photon has more energy than the red photon, and more than enough to kick an electron out of a metal.

Einstein's explanation of the photoelectric effect was just the start of an avalanche of discoveries that became quantum theory. In quantum mechanics, light is not just a particle and not just a wave: it is both, simultaneously.

The electrons in a hydrogen atom, which would normally be considered to be particles, have to behave like waves for our model of the atom's structure to work. The wave-particle duality of both electrons and photons is a fundamental tenet of twenty-first-century physics. It gave rise to a new, integrated mechanics, quantum mechanics, which supercedes Newton's classical approach and treats both photons and electrons as simultaneously waves and particles.

FOR GREATER UNDERSTANDING

Questions

1. What does Newton's first law say?
2. Describe a frictionless environment with which you have experience.
3. Recall the metric units of energy. Can you demonstrate to yourself that the definition of work, $w = -F \times d$, gives work the same units as energy? (Recall Newton's second law, $F = ma$.)
4. How is light different from the other common waves with which we are familiar (for example, water, sound, and shock)?
5. What did Bohr's model of the hydrogen atom require of the electron in the atom? What did Einstein's explanation of the photoelectric effect require of photons of light?

Suggested Reading

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Other Books of Interest

Holzner, Steve. *Physics for Dummies*. Hoboken, NJ: Wiley Publishing, 2006.

Websites of Interest

1. The Department of Physics and Astronomy website at Georgia State University provides information and graphs on blackbodies. —
<http://hyperphysics.phy-astr.gsu.edu/hbase/mod6.html>
2. The University of Oregon's *21st Century Science* website features information on Planck's constant and the work of Niels Bohr. —
http://abyss.uoregon.edu/~js/21st_century_science/lectures/lec12.html
3. The Beloit College (Beloit, WI) Chemistry Department website features a color view of the emission spectra of the elements. —
http://chemlinks.beloit.edu/BlueLight/moviepages/em_el.htm
4. The Biology Department at Pennsylvania State University provides an interactive table of the elements showing the spectra of the elements as they are selected. —
<http://chemistry.bd.psu.edu/jircitano/periodic4.html>

Lecture 7

“Seeing” Nanostructures

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 4: “Interlude Two—Tools of the Nanosciences.”

How can nanomaterials be “seen”? There are scanning techniques, three of which depend on an ability to put nanostructures on specific substrates and distinguish the nanostructures from the substrate, and spectroscopic techniques that depend on the quantum mechanical properties of electrons.

The nanotech revolution did not begin until late in the twentieth century, because it had to wait until the tools were developed to measure and manipulate nanoscale devices. Moving nanoscale items requires nanoscale tools. The history, design, and functionality of four techniques used at the nanoscale are the focus of this lecture.

Scanning Probe Instruments

Scanning probe instruments helped to launch nanotechnology. In the early 1980s, scientists working for IBM in Zurich, Switzerland, conceived of building an instrument based on the simple idea of gently dragging your finger across a surface. Even with your eyes closed, you would be able to tell the difference between a brick, a slab of granite, and a piece of carpeting. Your finger responds to the forces acting between it and the surfaces with which it is in contact, and it is sufficiently sensitive to tell the difference.

Of course, if you want to measure nanometer-size features on a surface, you need a tip that is nanometer or smaller in scale. How do we make such tiny tips? Think of things you know that form sharp points—icicles, stalagmites, drawn molten glass, and spun sugar.

Scanning probe tips can be formed in the same way that icicles form. A sample of the material can be heated until it melts and allowed to flow slowly into an environment held at a temperature below its freezing point. If the flow rate and cooling rate are properly set, little icicles of tip material form. Once they have cooled sufficiently they can be broken off and used in an appropriate scanning instrument.

In contrast, stalactites and stalagmites form when water evaporates from drops of a saturated solution. Stalactites hang down, and stalagmites form on the floor underneath them. Since both stalactites and stalagmites can form tapered points, either could be used as a nanoscale tip.

One could also make nanoscale tips from larger pieces of material by carving or slicing tiny pieces from the larger bulk material. But this would require a very sharp cutting instrument. Or you could make tips by building

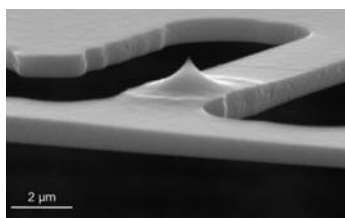
very tiny molds and pouring fluid material in and letting it cool to solidify. Or you might use a material that needed to be placed into the molds and heated to bake it into shape.

Atomic Force Microscopy

The specific method used to create a nanoscale tip depends on the material used, which in turn depends on the property of the surface to which the scanning probe instrument is sensitive. One of the early scanning tip methods is called atomic force microscopy. In atomic force microscopy (AFM), the scanning tip is generally made of either silicon or silicon nitride. The tip is mounted on a cantilever. When the tip is brought into contact with a surface, the cantilever is deflected according to the force exerted by the surface on the cantilever tip. Cantilevers are designed to deflect in proportion to the force encountered. The movements of the cantilever are monitored by scattering a highly collimated (aligned) laser beam off the top of the cantilever. The beam is deflected to a set of photodiodes. The photodiodes produce an electrical signal when photons fall on them, and the amount of current in each photodiode can be deconvoluted to give the position of the cantilever as it moves over the sample.

You might wonder how the laser beam can record motions of the tip on a scale as small as a nanometer. The reflection of the laser beam off the top of the cantilever magnifies the motion to make it easier to detect than you might expect. Imagine you have a laser pointer shining on a standard piece of paper about 10 cm from the end of the pointer. If you wiggle the laser pointer up and down, you can see the beam move up and down on the paper. Now move the paper much farther from the laser pointer. The same wiggle that caused the beam to move to the edges of the piece of paper at 10 cm from the pointer now sends the light way past the edges of the paper.

There are typically two different modes of AFM operation, “dragging” and “tapping.” Dragging works okay with suitably soft or flexible surfaces, but it might damage the tip or the surface if you applied too much force or if you dragged it across a rough surface. In AFM, the dragging mode is called “static mode” or “contact mode.” In contact mode, the risk of damage to the tip is minimized by maintaining a constant low force between the tip and the surface. The cantilever is physically moved to adjust the height of the tip above the material using an electrical feedback circuit as the adjustment mechanism. The position of the



Source: IBM Corporation/STM Image Gallery

A micrograph close-up of a nanoscale silicon atomic force microscopy tip. It measures 500 nanometers in length and only a few nanometers at its apex. It is attached to a cantilever that controllably scans the surface of the substrate material with the accuracy of one nanometer (one millionth of a millimeter). Image originally created by IBM Corporation, 2010.

cantilever therefore tells you something about the surface over which the tip is passing.

If your picture of atoms is that they resemble little billiard balls and that a solid consists of a regular pattern of these balls, this is a good time to dissuade you of that notion. The AFM process works because both atoms and the solids they form are “soft” on a nanoscale. The electrons that form the outer edges of the atoms and the bonds between them do not form a rigid boundary. As long as the tip maintains a slightly negative electrical potential relative to the solid, it will be repelled by the atomic or solid surface. The electrical repulsion allows the tip to scan the surface at a constant distance from it. The tip is not actually in contact with the surface in a macroscopic sense.

The second mode of AFM operation is the tapping mode, where the tip would bounce up and down at a constant frequency as it moved over the surface. In more technical terms, this mode is considered to be a “dynamic” or “noncontact” mode. The cantilever itself is oscillated at just above its natural resonance frequency. The cantilever has a resonance frequency in the same way a tuning fork or a guitar string has a resonance frequency. The amplitude of the oscillation is usually 1 to 10 nm. The force exerted by the electronic structure at the surface of the sample being investigated damps the oscillation of the cantilever. A feedback loop serves to maintain a constant cantilever frequency by adjusting the height of the cantilever above the surface in response to the damping. In this way, the average position of the tip maps out the topography of the surface of the material being investigated.

Scanning Tunneling Microscopy

Another nanoscale microscopy is scanning tunneling microscopy (STM). STM depends for its very existence on the quantum properties of electrons and nanoscale structures. In normal electrical circuits, the voltage, or driving force of the electricity, is equal to the current times the resistance. The current can be thought of as the charge moving past a point in the circuit every second, and the resistance can be thought of as the friction between the moving charges and the material through which the charges are moving. Symbolically, the relationship is summarized by the equation $V = IR$. The direct relationship means that doubling the resistance or friction requires a doubling of the voltage, or a doubling of the driving force, to maintain a constant current. Or, if the resistance stays the same, the current will double when the driving force doubles. The mathematical equation is called Ohm’s law, based on his experimental observations in the 1820s.

The scanning part of the technique is identical to that in the AFM technique. The microscopy means that we are looking at something on the microscopic scale—or smaller—when we consider the nanoscale. It’s the tunneling part that is specifically quantum here. STM monitors the current

flowing between a tip and the surface. However, STM measures current under conditions where Ohm's law says the current should be zero—the resistance is so large that the voltage is not capable of pushing any current through the system. But in STM, current is measured because of a quantum mechanical property called “tunneling.” Tunneling sounds like it is impossible, but it is observed in a variety of environments.

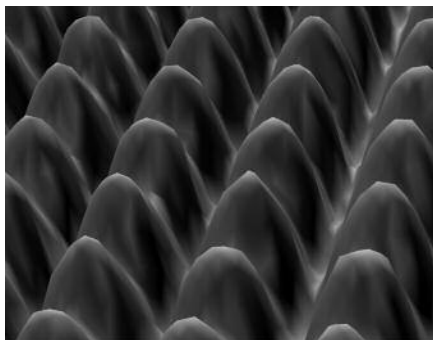
Imagine there are a bunch of tennis balls at the bottom of a pit. You want to get the tennis balls out, but the pit is too deep for you to reach any of the balls. Here the tennis balls are the electrons, the depth of the pit is the resistance, and the flow of electrons out of the pit, the current, is zero.

According to Newton's classical mechanics, gravity keeps the tennis balls at the bottom of the pit, and none of them can ever bounce out. A physicist would tell you that the force of gravity is balanced exactly by the force exerted by the ground or the lower level of tennis balls to keep the balls fixed. You would have to do work to get the tennis balls out of the pit.

However, if tennis balls were capable of tunneling, then it would be the case that occasionally one would just pop up out of the pit. Sounds ridiculous, doesn't it? But that is quantum mechanics. First of all, quantum particles are in constant random motion. So the first correction we should make to our mental picture is to allow the tennis balls to be dancing around perpetually, like water droplets on a hot, oiled pan. If this were the case, it becomes conceivable that every once in a while a tennis ball near the top of the collection of tennis balls could be bounced out of the pit. The more tennis balls, the higher the possibility that a tennis ball will come out.

In STM, the electrons in the material being examined act like the tennis balls in a pit. The tip on the microscope acts like the extender arm that is just a little bit too short to actually reach down to the surface of the tennis balls and grab one. But if the tennis balls are in constant random motion, then the surface of the tennis balls is not fixed; it is moving, more like the surface of the ocean than the land. In this circumstance, occasionally one tennis ball bounces high enough and near enough for a very agile grabber to grab it. It shouldn't happen according to classical mechanics, because the arm is too short to reach deep enough to grab a tennis ball—but because of the motion of the tennis balls, it can happen.

There's another way to think about tunneling. Quantum mechanical particles behave like waves even while they have the properties of particles.



Source: IBM Corporation/STM Image Gallery

An STM picture of a perfect nickel surface. Image originally created by IBM Corporation, 2010.

Ocean waves are a reasonable model to invoke here. If you are out in a boat on the open water, you can usually stay dry. But even on a relatively calm day, waves can occasionally spray you with water, or even dump a bucketful of water in the boat. Waves are less predictable in their behavior than particles.

The probability of finding an electron in a location where it does not have enough energy to be is small, but it is not zero. When electrons move through a space where Ohm's law says the current should be zero, then we are observing tunneling. Today, we have sophisticated instruments that can record very small currents associated with the movement of very few electrons through space and allowing STM to be a useable technique for observing nanoscale features of surfaces.

Scanning Electrochemical Microscopy

Other properties of materials can be monitored through scanning techniques to image surfaces at the nano scale. The chemical reactivity of a surface can be monitored using a technique called scanning electrochemical microscopy. Electrochemistry is the name given to a category of chemical reactions that are accompanied by the transfer of electrons from one chemical species to another.

In scanning electrochemical spectroscopy, the materials to be studied and the tip monitoring their behavior are both placed in an electrolyte solution. Electrolyte solutions contain a liquid or molten solvent and ions, chemical species that have an electrical charge and are free to move in the solvent. The electrolyte provides one of the reagents required to cause a chemical reaction. The other reagent must be a component of the surface. The electrode tip in this technique is maintained at an electrical potential that promotes a chemical reaction at the surface when the tip, or electrode, is sufficiently close to a reacting species on the surface. When the reaction occurs, charges move through space and the tip records a current. In this way, scientists can map out the reacting sites on any surface. As in STM, scanning electrochemical spectroscopy allows scientists to image the topography of a surface or its surface reactivity.

One can also take advantage of the magnetic properties of material to look at surfaces using magnetic force microscopy. The tip at the end of the cantilever is the same as an AFM tip but coated with a magnetic material, often either nickel (Ni) or cobalt (Co).

Scanning techniques used in an oscillating or tapping mode can have increased sensitivity over static mode measurements. A signal is recorded as the difference between the expected oscillation pattern and the actual pattern. In the same way that it is easier to see a single goose leaving or joining a group of geese than it is to determine the number of geese in the gaggle, it is sometimes easier to detect minute changes in electrical responses than it is to measure the absolute electrical response.

Spectroscopic Techniques

Spectroscopic techniques involve using light to investigate chemicals. Only a very small portion of the electromagnetic spectrum is visible to the human eye. According to our classic understanding that light is a wave, the energy of light is directly proportional to its frequency and inversely proportional to its wavelength. The wavelength of visible light ranges from about 400 to 750 nm. Blue light, at the lower end of this range, near 400 nm, provides more energy per photon than red light, which has wavelengths near 750 nm. The energy of all visible light is generally smaller than the energy required to break a chemical bond or initiate a chemical reaction. Visible light interacts with individual chemical particles in one of two ways—by being absorbed or emitted or by being scattered.

Because of the conservation of energy, any chemical that absorbs visible light ends up at higher chemical energy. This energy usually results in an increase in electrostatic potential energy for one of the electrons in the chemical. The electron moves from its ground electronic state to an excited electronic state. In atoms, this means that the electron has taken the energy it was given to move further away, on average, from its nucleus than it was in the ground state. In nanoparticles, this concept still applies, but it is sometimes difficult to illustrate what is meant by “further away,” because there are many nuclei, not just one.

One class of nanoparticles, quantum or nanodots, are able to interact with light and reveal features of their structures depending on the wavelengths of visible photons they absorb. Quantum dots are either nanoparticles composed of pure metal atoms, or composites with a core of a semiconductor material, commonly Cd-Se (cadmium selenide) with a surface shell of ZnS (zinc sulphide). The color of a nanodot is often related to its size, more specifically to its surface area.

Nanodots have also been successfully “functionalized” to be used in a variety of biomedical applications. One spectacular use of nanodots is in photodynamic therapy for certain types of tumors. One problem with chemotherapies for cancer and other diseases is that the same medicine that kills the cancer cells can kill healthy cells. The holy grail of cancer treatment is to identify a treatment method that attacks only cancer cells. Functionalized nanodots are nanodots chemically bonded to proteins that are selective in attaching to cancer cells in the body. The nanodots therefore get concentrated in the vicinity of the tumor. Since the dots absorb a specific color of light, the absorption can be used to locally heat and kill the cancer cells in tumors close to the skin. A laser can deliver a burst of the right color of visible energy. The light is absorbed by the nanodots, causing a local increase in temperature sufficient to kill the cells in their immediate vicinity. But if the color light is not absorbed by the body, the light that does not strike a nanodot directly simply passes harmlessly through the body.

Electron Microscopy

Another way that light can tell us about the structure of nanomaterials is by scattering off them. In the same way that X-rays reveal broken bones to a doctor, chemists can monitor the scattering of X-rays to determine the structure of nanomaterials. This methodology is of limited use with nanomaterials, however, because of the inverse relationship between wavelength and energy. For nanomaterials that are 100 to 500 nm in dimension, then, we need light that is no longer than 100 to 500 nm in wavelength. Unfortunately, as the features get smaller, the light appropriate to look at them becomes higher and higher in energy, which can destroy the surface to be examined.

Photons may not do a good job of illuminating nanoparticles—but remember, electrons have wavelike properties, too. The energy of an electron, though, depends on both its mass and wavelength. The wavelength is determined using h , Planck's constant, divided by $m \times v$, the mass of the electron times its velocity. Because of its charge, an electron is pretty easy to accelerate to any velocity you like. An electron with a wavelength of 100 nm is traveling at a velocity of 7.3×10^3 m/s, but carries only 2.4×10^{-23} J of kinetic energy, in part because it has a very small mass. In contrast, a single 100 nm photon carries 2.0×10^{-18} J of energy—100,000 times more than the electron. This explains why short wavelength photons are so destructive.

Photons scatter off atoms and molecules by interacting with their oscillating dipoles. Electrons scatter off atoms and molecules by interacting with their charge distributions. Electron microscopes can utilize electron waves that are short enough to see nanoscale features without destroying the objects with which they are interacting. And they directly show the charge distribution that determines the chemistry of the structure. These two characteristics make electrons very useful in the nanoscopic investigations of nanomaterials.

FOR GREATER UNDERSTANDING

Questions

1. What do the acronyms AFM and STM mean?
2. How is STM different from all the other methods of “seeing” nanostructures discussed here?
3. How do AFM and STM instruments convert their nanoscale information into information we can interpret?
4. What is spectroscopy?
5. What is the advantage of electron beam microscopy over light spectroscopy for investigating nanomaterials?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

Eaton, Peter, and Paul West. *Atomic Force Microscopy*. New York: Oxford University Press, USA, 2010.

Websites of Interest

1. Peter Eaton and Paul West established the *AFMHelp* website to accompany their book *Atomic Force Microscopy*. The website features an image gallery including an image of gold nanotriangles. —
http://afmhelp.com/index.php?option=com_joomgallery&func=detail&id=9&Itemid=76
2. Nanoco, Inc. (Sigma-Aldrich Materials Science) provides an informative website about quantum dots used in nanoprocesses. —
<http://www.nanocotechnologies.com/content/Products/CadmiumBasedQuantumDotsNanoDots.aspx>

Lecture 8

Building Nanostructures

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 4: "Interlude Two—Tools of the Nanosciences."

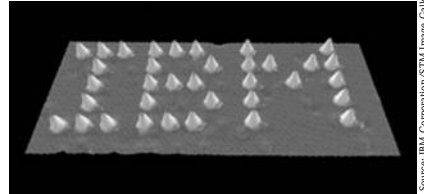
Pushing Atoms and Molecules

The first atom-by-atom construction of a nanoscale structure was reported in 1990. Donald Eigler and Erhard Schweizer used a scanning tunneling microscope (STM) to push a set of thirty-five xenon atoms to spell out "IBM" on a nickel surface. After using the tungsten needle tip to assemble their structure, they used the same device to record a picture of it. The tip is lowered to a fraction of a nanometer above the surface being examined. A slight difference in voltage between the tip and the object allows a small current to flow, even though the tip never touches the surface.

Because of the weakness of the interaction between xenon atoms and metal surfaces, the nickel was maintained at a very low temperature, just a few degrees above absolute zero, to prevent the xenon atoms from being bounced off the surface due to thermal vibrations in the metal. Eigler and Schweizer began building the initials by spraying xenon atoms at a chilled crystal of nickel, in a vacuum, leaving a random pattern of the atoms on the surface.

Just five years later, in 1995, scientists at IBM-Zurich precisely positioned individual molecules at room temperature for the first time ever. This was accomplished by attaching four bulky hydrocarbon groups to a rigid molecule. The hydrocarbons formed sufficiently strong interactions with the surface to prevent thermal surface vibrations from bumping the molecules out of place. The interactions with the surface were still weak enough to allow the molecule to be pushed into specific positions by the STM tip.

Then in 1998 came the report of the fortuitous observation of the first "molecular wheels"—propeller-shaped molecules that rotate rapidly in a bearing-like structure formed by surrounding molecules on a surface. The molecules can switch between two states—rotating and immobilized. The rotation of the molecular wheel was observed to occur at high-speeds using an STM. An irregularity in the surface underneath the wheel provided a bearing allowing it to rotate. When placed instead on a perfectly ordered



The first atom-by-atom nanostructure. Image originally created by IBM Corporation, 1990.

Source: IBM Corporation/STM Image Gallery

substrate, the other absorbed molecules stopped the rotation. The wheel demonstrated an essential component in the effort to construct nanoscale molecular engines. Perfection was the enemy.

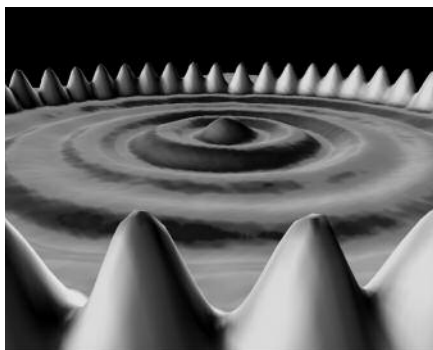
One of my favorite STM pictures was first published by IBM researchers in 1993. It shows a ring of 48 iron atoms on a copper surface. The ring has a radius of about 7 nm. The picture clearly shows the standing waves due to variations in the density distribution of surface state electrons exactly as one would predict from the application of quantum mechanical principles.

But as interesting as these structures are, they are really just scientific curiosities. No company in the modern era can afford to produce products one at a time. To be economically viable, nanotechnology needs to be done using mass-production techniques. Pushing individual atoms and molecules into place just won't cut it.

It is possible to make nanodevices using a top-down approach. Top down means you start with a large piece of material and cut it into the final product. The top-down approach appears to require us to be nano Michelangelos, using nano tools to sculpt nano-sized features out of a block of raw material. For instance, we could take a slab of pure silicon, carve nanometer-sized canals in its surface and fill the canals with silicon dioxide and the other elements needed to make nanoscale integrated circuit components. We could cut nano pieces of gold off an ingot of gold to make conductive connectors for our integrated circuit.

There are two problems with simply chopping big pieces into nanoscale chunks. First, nanoscale chisels and hammers are hard to come by, and second, the result would be a large amount of waste material. Our toolbox for creating nano features includes three tools—force microscopes, laser beams, and chemical reagents. Within these constraints, how can we efficiently generate nanostructures using a top-down approach?

One type of top-down approach uses an AFM to physically etch a surface. The tip of the device can score a resist or a substrate, leaving a scratch or impression in it. Extremely hard tips of platinum-iridium or diamond are particularly effective, but this technique is currently limited by the sharpness and hardness of the tip. Like a kitchen knife, a good tip becomes blunt over time, thus reducing its accuracy and ability to effectively create nanoscale features.



Scanning tunneling microscopic view of 48 iron atoms on a copper surface. Image originally created by IBM Corporation, 1993.

Source: IBM Corporation/STM Image Gallery

Another top-down pattern technique applies a voltage between the tip of an STM and a surface. The voltage permits a transfer of materials from the tip to a surface and vice versa. For example, researchers have used STM to deposit or remove nanometer mounds of metals from surfaces, including gold, platinum, and silver. They have also anodized metals like aluminum and titanium to create thin protective layers on the metallic surface. A layer on a surface can also be removed using this technique. For example, when silicon is exposed to air, it forms a thin, insulating layer of silicon dioxide on its surface. Dipping the silicon in hydrofluoric acid removes this rust-like layer and replaces it with a thin layer of hydrogen atoms. By placing a scanning probe near the surface of the sample and applying a voltage, scientists can remove the hydrogen and create a pattern in the silicon surface. The pattern of dots or lines forms when the exposed areas reoxidize.

Twenty-first-Century Lithography

Lithography has been an accepted macroscale printing technique for hundreds of years.

Currently, metal oxide semiconductor transistors for computer chips are made by a series of steps involving oxidation, chemical depositions, and lithographic techniques.* To make a set of chips you begin with a single piece of silicon. By heating it in an oxygen atmosphere, the surface of the silicon is converted to silicon dioxide. Then it is heated in an atmosphere of ammonia and SiH_4 to deposit a layer of Si_3N_4 . Then a photographic mask is applied. The mask acts like traditional silver photographic masks. UV light shines through the mask. Where the mask is transparent, the emulsion is weakened by absorption of the energy for the UV light. It is then removed by a chemical solvent, which leaves the unirradiated emulsion intact. The exposed Si_3N_4 is etched by exposure to beams of reactive ions, revealing the SiO_2 layer underneath. Then the remaining emulsion is removed by a strong chemical solvent. These steps are repeated until an appropriate set of conducting Si material and insulating SiO_2 material is built into an appropriate configuration. High-energy dopant molecules bombard the structure and are absorbed into thin SiO_2 layers, leaving conducting materials behind and producing the source and drain of the transistor. Finally, metal atoms are deposited on the surface, and they are etched and covered to create the connections between the transistor and the rest of the world. If you start with a large enough piece of silicon and small enough masks, it is possible to make millions of separate chips simultaneously using these techniques. But small as these are, they are not nanoscale. At the nanoscale, light in the X-ray regime must be used, and X-rays are too short in wavelength and too high in energy to behave properly in the presence of the masks—they diffract around them and deliver Mack-truck-scale impacts

* Animations of several nanoscale lithography processes are available at the University of Virginia *Virtual Lab* website cited on the “For Greater Understanding” page of this lecture.

to the surfaces they encounter. Neither characteristic recommends using X-rays to create neat lithographic nanomaterials.

Macroscopic lithography is well known to both artists and printers. Lithography depends on drawing an image using wax or oil on an etched surface historically of stone, but now often of aluminum. The wax or oil forms a hydrophobic layer that preferentially attracts ink, while the etched surface contains ionic species and is therefore hydrophilic or water-loving, and attracts water in preference to oil. Lithography is a robust technique, and one lithographic plate can be used repeatedly to make many copies of the object drawn on it.

Over the past thirty years, creative scientists have devised modifications of lithography that work at the nanoscale. These approaches can be extremely efficient. Because they can be easily converted to massively parallel implementation, they can also increase our ability to automate the manufacturing process for many different nanoscale devices. The techniques include optical lithography, X-ray lithography, and electron beam lithography. If we consider paralleling traditional lithography to make nanostructures, we need to identify an ink, a way to create nanoscale etchings, and a method for creating the print that we want. In this arena, we are making some progress at doing things on the nanoscale.

At Harvard University, George Whitesides and his collaborators have developed a technique called micro-imprint lithography. On the nanoscale, they replicate an old-fashioned rubber stamp. A rigid mold containing the nanoscale pattern is prepared and pressed into a resist spread on a surface. The resist is heated so that it softens and can flow so it is easily deformed to exactly match the mold's profile. When the temperature drops, the resist goes through a phase change and becomes essentially a rigid solid.

Molds can be made of a variety of materials, including silicon and silicon dioxide. They are made through conventional electron beam lithography techniques, but they can be used to form lots of resists. Polymethyl methacrylate, a polymer also found in hard contact lenses, makes a good resist because it does not expand too much when heated or contract too much when cooled, so it maintains the shape pressed into it by the mold. Reactive ion etching with oxygen can be used to remove the thin compressed layer of residual resist from the substrate. Whitesides's group reported successful printing of 10 nm resolved features over a print size of 15 x 18 mm.

Another version of nanoscale lithography is dip-pen lithography. First developed by Mirkin and collaborators at Northwestern University, dip-pen nanolithography uses AFM tips to write on surfaces with nano ink. The technique is quite flexible and can be used to write features as large as 10 micrometers or as small as 50 nm. Inks used include organic compounds, biomaterials such as DNA, lipids, and proteins. Thiols, sulfur-containing compounds, and

inorganic compounds containing metals can also be used. Nanoink products are used in protein analysis and bioengineering applications.

In December 2010, the *Nanowerk News* website reported that a group of Beckman Institute researchers at the University of Illinois had discovered a practical method for writing metal lines less than five nanometers (5 nm) wide, a big step in creating contacts to and interconnects between nanoscale device structures like carbon nanotubes and graphene that have potential uses in electronics applications. The research was led by Joe Lyding (with his student Wei Ye as lead author), Gregory Girolami, and Angus Rockett of the Beckman Institute for Advanced Science and Technology. Recent research by Lyding's group has demonstrated methods for depositing graphene on semiconducting substrates and creating semiconducting carbon nanotubes that make it possible to incorporate carbon-based materials into electronics and other devices that now rely on silicon and metals to operate. The researchers report their technique for the patterning of metallic nanostructures on surfaces. Eventually, they hope the method will allow controlled fabrication of nanoelectronics and quantum devices.

The researchers write that "Current top-down fabrication technologies used in industry involve conventional lithographic processes, which are approaching their fundamental size limits." Responding to the current challenges involving fabrication at scales smaller than 10 nm, they have demonstrated "the ability to write metal lines that are less than 5 nm wide."

To do this we use the electrons from our STM tip to "crack" molecules that are introduced in the gas phase to the STM tip-sample junction. The procedure of using STM electrons to break apart molecules and yield a metallic deposit is not new; however, previous attempts have been plagued by high levels of carbon impurities in the deposits and metallic behavior had not been demonstrated.

To our knowledge this is the first demonstration of sub-5 nm metallic nanostructures in an STM-EBID experiment, and it opens new opportunities for making deterministic molecular scale metallic contacts.

Letting Chemistry Be Chemistry

A true bottom-up approach requires the assembly of structures one atom at a time. We have to figure out the atoms we need and a way for them to stick together. Just as in the macroscopic world, this can be a time-consuming process. But bottom-up approaches can be 100 percent efficient. Using every atom reduces waste to zero. There are very few traditional macroscale chemical-synthesis techniques that claim 100 percent efficiency.

The big complication in bottom-up manufacturing is the same problem that chemists using traditional synthesis techniques encounter—some materials are pretty happy to stick together and some need a good strong glue to hold them together.

Lots of stone walls in New England have existed for one hundred years or more even though they are dry stacked with no mortar. To assemble a bottom-up nanodevice, we need to find atomic or molecular “stones” to use. If we only find the atomic equivalent of bricks, then any glue we would use to mortar the bricks together would have to be the same size as the actual components of the device—and that much glue would affect the structure in an essential way, because it would not be a minor component of the structure.

The surfaces that accept our nanostones turn out to be a critical component of the nanostructure. Usually they are made of single crystals so they are very regular in their surface topography. And we usually need to keep them cold to reduce vibrational activity because a vibrating surface can make it impossible to assemble a nanostructure. The first nanostones used were xenon (Xe) atoms. Xenon is the largest stable noble gas. How should we move these Xe atoms into place? In 1989, Donald Eigler figured it out when he assembled thirty-five xenon atoms to spell out the letters “IBM.” Later, when Eigler assembled a corral of forty-eight iron atoms, the corral confined some valence electrons on the surface of the copper, enabling him to experimentally confirm that the electrons displayed exactly the wave properties expected from basic quantum calculations on confined electrons.

But so far, nanostones have only been used to create curiosities. The lack of a sufficiently strong chemical bond between the surface and the nanostone means that the structure is not strong enough to do anything useful. So let’s reconsider nanobricks. A few years ago I built a small retaining wall against a steep slope at the side of my house. The bricks I bought to build the wall were custom shaped to interlock and hold together. Once I put the first course in, the rest went together like a puzzle, and each course locked into the one below. There is no mortar in that wall, but it is solid and has maintained its structure. Could we find molecules like those custom-shaped bricks? If we could, it might be possible to build fairly sophisticated structures without requiring any mortar.

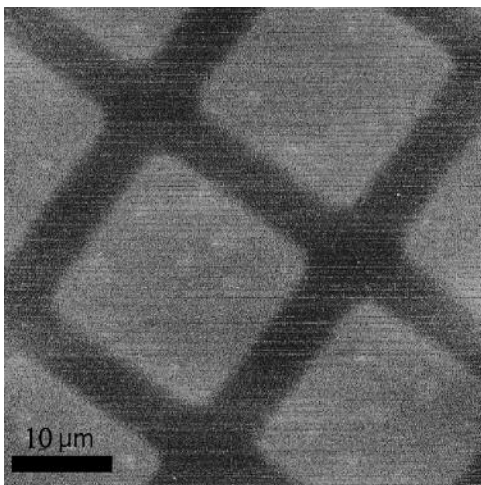
Scientists today use the innate attractions between molecules as a sort of mortar to hold sophisticated structures together. One example of a nanobrick is a molecule called an alkane thiol. The “alkane” part of the name refers to a covalently bonded molecule made of carbon and hydrogen. The carbons form a chain, and each is connected to an appropriate number of hydrogens to fill its valence. The “thiol” part of the name means that there is a sulfur atom attached to the last carbon at one end of the alkane chain. The sulfur end has a strong attraction to gold and a weaker attraction to some other metals. So we could take a piece of gold only several nanometers thick, or a solution containing some gold ions, and convince a single layer of alkane thiols to attach themselves to the gold. If we mix the gold and the alkane thiol together in the presence of the proper helpers, we don’t even need to lift the alkane thiol bricks to put them in place. They will float in the solution

and, because of the strong attraction between the thiol and the metal, they will fall into the correct position, generating a single layer of alkane thiol on the surface of the gold particle.

Furthermore, because the alkane part is not particularly attracted to the metal but prefers to be near other alkanes, the alkane molecules stand up off the surface like kelp floating up from the ocean floor. The attraction between the gold and the thiol is sufficiently robust to resist the normal vibrations at room temperature; once we make the single layer of thiol, it pretty much stays put. Any structure that

assembles itself because of the specific attractive forces between the brick and the surface is called a “self-assembled” monolayer (SAM).

Ultimately, self-assembly will become the most attractive approach to creating nanostructures. Why? Because it requires so little work on our part. The work is done by the intermolecular forces acting to move our component compounds to minimum energy configurations. As is so often the case, we have learned the art of self-assembly from Mother Nature. Her cell walls, constructed of lipids with nonpolar hydrocarbon tails and polar head groups, self-assemble into bilayers in aqueous environments. The structure forms because the linear, nonpolar tails want to align next to each other, and the polar head groups that are attracted to the polar water molecules arrange themselves on the inner and outer surfaces.



The patterning of self-assembled monolayers (SAM) was photographed by scientists at the University of Leeds in the United Kingdom.

© University of Leeds/Kevin Crithley

FOR GREATER UNDERSTANDING

Questions

1. What is the advantage of nanolithography over atom-by-atom assembly?
2. What is the difference between top-down and bottom-up nanoassembly?
3. What is a major advantage of the bottom-up approach?
4. Copper atoms have an atomic radius of 128 pm. If you wanted to make a copper wire that was 5 nm wide, how many copper atoms wide would the wire be? How close is this to Feynman's picture of how we could write the entire contents of all the books ever written on the head of a pin?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

Jackson, Mark J. *Micro and Nanomanufacturing*. New York: Springer Science+Business Media, 2010.

Articles of Interest

Ye, Wei, Pamela A. Peña Martin, Navneet Kumar, Scott R. Daly, Angus A. Rockett, John R. Abelson, Gregory S. Girolami, and Joseph W. Lyding. "Direct Writing of Sub-5 nm Hafnium Diboride Metallic Nanostructures." Washington, DC: American Chemical Society. *ACS Nano*. Vol. 4 (11), pp. 6818–6824, 2010.

Websites of Interest

1. The University of Virginia Virtual Lab website provides information on their program and several videos on nanoscale lithography. — <http://www.virlab.virginia.edu/VL/home.htm>
For Optical Lithography:
<http://www.virlab.virginia.edu/VL/Photolith.htm/state/1>
For Projection Electron Lithography:
<http://www.virlab.virginia.edu/VL/Scalpel.htm>
For Extreme UV Lithography:
<http://www.virlab.virginia.edu/VL/EUV.htm>
2. The IBM *STM Image Gallery* website features images from structures at the nanoscale. — <http://www.almaden.ibm.com/vis/stm/lobby.html>
3. The *Nanowerk News* website provides recent information on nanotechnology from around the world. — <http://www.nanowerk.com>

Lecture 9

Nanoscale Sensors

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 7: "Sensors."

How will nanotechnology be used? Building nanoscale sensors designed to detect the presence of specific chemical or biological entities and signal their presence is one process being investigated. Human senses depend on a variety of biological sensors. Our eyes are light sensors, our ears sense pressure variations, and our noses are perhaps the most sensitive of human sensors. What do these sensors have in common? All of them respond to an external stimuli in a predictable way, producing an electrical signal that is relayed by our nervous system to our brain.

A variety of macroscale mechanical sensors are used every day: thermostats that register air temperature and transmit electrical signals to furnaces and air conditioners to adjust the flow of warm or cool air; faucets that turn on when a hand is at the right proximity; and paper-towel dispensers that advance the roll of towels in a similar manner. Women around the world depend on home pregnancy tests to sense the biochemical changes that accompany the earliest stages of pregnancy.

All sensors, natural and man-made, have one thing in common. They detect something, perhaps something that usually escapes human senses and *transduce* or convert this detection into a signal that can be easily perceived.

Natural Sensors

A variety of naturally occurring chemical compounds can be used as *indicators*; they change color in the presence of specific analytes. Both phenolphthalein and litmus change colors when exposed to high concentrations of hydrogen ions. High concentrations of hydrogen ions are present in solutions called acids. Many other naturally occurring indicators exist (for example, pigments from red cabbage). Acid-base indicators are usually relatively large molecules that have specific locations where their hydrogens are quite labile; they are easily removed from the molecule when their environment does not contain many hydrogen ions and easily replaced when an excess of hydrogen ions are available. In many cases, the addition or removal of a single H^+ is sufficient to change the energetic environment of the electrons in the molecule or to alter the molecule's structure in three-dimensional space and affect the color of the indicator molecule.

How does this color change occur? The electrons in atoms and molecules are only allowed to occupy specific, quantized energy levels. In atoms the

energy levels are usually well separated from each other. Atoms can absorb or emit only photons of light that carry exactly the energy that corresponds to the gap between two of their allowed electronic energy levels. The resulting line spectra are quite sharp and distinctive.

However, when a large quantity of atoms are chemically combined to make molecules, the atomic orbitals get combined with each other to form molecular orbitals. Molecules with large numbers of atoms end up with molecular orbitals that are not sharply separate from each other but instead smear out into bands of allowed energies.

The electrons in an atom or molecule normally occupy a set of available energy levels so that the overall system has the minimum potential energy. Quantum mechanics restricts the number of electrons allowed in any given orbital. But in molecules, there are always more orbitals than needed to hold all the electrons. In terms of energy, there is a “highest occupied molecular orbital” (HOMO), which contains the last of the molecule’s electrons. The orbital at the next highest energy is called the “lowest unoccupied molecular orbital” (LUMO). The energy difference between these two is responsible for the color of the molecule. If the energy difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is in the range of energies corresponding to photons with wavelengths from 400 to 750 nm, the compound is seen as colored. If the difference is either larger or smaller than the energy provided by a visible photon, the molecule is not colored. The interesting thing about indicator molecules is that adding or removing just one hydrogen ion from the molecule causes the entire energy structure to shift, so that the energy gap between the HOMO and the LUMO changes. This change in the HOMO-LUMO gap causes the color change that is detected when a dye molecule is put in an environment containing lots of hydrogen ions. The shift in molecular orbitals is the transduction of the chemical change resulting from the addition of a single hydrogen ion.

In other environments there is a maximum energy above which electrons are no longer considered as belonging to the molecule. This is called the ionization energy. If a phenomena occurs that provides an electron with enough energy for it to escape its molecule, the molecule is considered to have been ionized. The electron is then free to move through space, outside the confines of its molecule. These free electrons can produce a current that can be detected using a variety of electrical phenomena. In this way, a molecular change is transduced to an electrical current. Instruments can be built that register even the smallest electrical currents, so this kind of transduction can be very useful.

Electromagnetic Sensors

Biological systems often provide an entire cascade of events that are registered as a signal transduction. Oftentimes, these begin with a specific event that binds two distinct molecules—a receptor and an analyte. The binding

process often requires that the receptor and analyte fit together like a lock and key. The binding either changes the three-dimensional arrangement of the analyte, forcing a change in its environment, or it changes the electrical environment sufficiently to provide an electron to carry the signal that binding has occurred.

The ideal chemical sensor produces a signal when it interacts with only one specific chemical entity. A smoke detector or carbon monoxide detector senses the presence of smoke or carbon monoxide and produces an earsplitting noise in response.

Smoke detectors typically rely on small samples of the radioactive isotope americium-241. The americium produces a predictable stream of alpha particles that ionizes the air between two plates hooked up to a battery. One plate is positive and the other is negative. The ions provide a current between the plates, which the smoke detector monitors. Smoke consists of charged particles. When smoke enters the region between the plates, the ions are attracted to the smoke, and the current between the plates drops. When the current falls below a minimum level, the alarm sounds.

Other smoke detectors depend on the photoelectric effect. In these, a light source is directed on a metal surface, producing photoelectrons that are measured. If smoke blocks the light, photoelectrons are no longer generated, the current drops, and again the alarm sounds. The problem with smoke detectors is that dust and cooking fumes can set off false alarms. Interference like this is a frequent complication in the use of sensors.

Carbon monoxide (CO) detectors can use several types of sensors. One mimics the behavior of hemoglobin in blood. CO is dangerous because it binds with hemoglobin more strongly than does oxygen. In a biomimetic sensor, a gel changes color when it absorbs CO. A small light source shines light through the gel and hits a photodiode detector. When the color of the gel changes, the amount of light passing through it changes, and the amount of light hitting a photodiode changes. The change sounds the alarm. Once a biomimetic sensor has changed color, it must be placed in a CO-free environment to reset itself.

Other CO detectors use metal oxide semiconductors as sensors. The metal oxide semiconductor has a high enough resistance that it normally does not conduct any current. However, if a sufficiently high CO concentration comes into contact with the semiconductor, the CO absorbs on to the surface of the semiconductor. The absorption lowers the resistance of the semiconductor, and it passes a current. The flowing current causes the alarm to sound. Carbon monoxide has a distinctive chemical signature. Therefore, carbon monoxide sensors are less subject to false alarms than most smoke detectors.

Some sensors undergo mechanical deformations in response to physical changes in their environments rather than to chemical changes. In older

home alarms, an actual metal-to-metal contact allowed a current to pass continuously. It was only when the contact was broken and the current stopped that the alarm sounded. A power failure could also set off a false alarm in these simple systems.

Biosensors

In the same way that macroscopic sensors respond to changes in their environment, nanoscale sensors can be designed to respond to either mechanical or chemical changes. Because of their small size, chemical nanosensors might be optimized to respond to the presence of a single molecule of an analyte. This would represent the ultimate sensitivity of any sensor. However, many analytes are closely related to one another both chemically and physically. A more sophisticated and potentially more accurate approach to distinguishing among closely related analytes is to establish a matrix of tests. If the entire set of tests is run on an analyte, examining it from a variety of different perspectives, the aggregate result is more likely to identify the analyte present. Use of nanoscale sensors will significantly simplify the matrix approach by minimizing both the size required to assemble the matrix and the quantity of analyte required for the tests.

Under other circumstances, sensors may be needed to provide a calibrated response related to the concentration of an analyte present. Whether sensing mechanical changes, the presence of one molecule, or the concentration of molecules, it is hoped that the sensor would produce the exact same response every time it detected the analyte of interest.

Electronic “Noses”

Exciting progress in developing new sensors is being made at the Monell Senses Institute in Philadelphia. In 2005, Monell researchers working with scientists from the University of Pennsylvania used carbon nanotubes coated with DNA to create tiny sensors able to detect molecules associated with odor and taste. Among the molecules the device was able to “smell” was dinitrotoluene, a chemical component of military-grade explosives. The sensor was made of two pieces—a detector and a transmitter.

What we have here is a hybrid of two molecules that are extremely sensitive to outside signals: single-stranded DNA, which serves as the “detector,” and a carbon nanotube, which functions as “transmitter.”

Put the two together and they become an extremely versatile type of sensor, capable of finding tiny amounts of a specific molecule.*

These devices depend on a small change in the electrical environment of the DNA attached to the carbon nanotube when an analyte binds to it. The

* Staii, Cristian, Alan T. Johnson, Jr., Michelle Chen, and Alan Gelperin. “DNA-Decorated Carbon Nanotubes for Chemical Sensing.” *Nano Letters*, vol. 5, iss. 9. Pp. 1774–1778. September 2005.

nanotube amplifies the electrical change, transducing it into a detectable signal. The DNA is engineered to respond specifically to the analyte of interest. The nanotube is a hollow tube of carbon atoms that is an excellent conductor of electricity. In principle, there are no limits to the molecules these devices could be designed to “smell.” They could identify molecules from explosive devices, poisons, cancerous tumors, or any airborne pollutant.

Similar detectors could be designed to sense compounds produced when foodstuffs carry disease organisms. Food packages could contain labels impregnated with nanosensors that change color when dangerous compounds are present. Supermarket managers could tell on a package-by-package basis which samples of produce or meat contained *E. coli* bacteria, or the deli manager could identify egg salad carrying salmonella.

Other Nanosensors

Nanotechnology can also produce improved photonic sensors, which convert optical information to digital form. A digital camera can be improved by nanoscale devices because smaller pixels mean a higher-resolution image. Nanoscale sensors also promise the possibility of fabricating defect-free devices, so photos could be larger and more accurate. In a communication network, photonic sensors would improve conversion of optical data into electricity, supporting faster and more accurate data transmission.

Nanoscale vanadium dioxide changes from a transparent state to a reflective, mirror-like state in less than 100 femtoseconds as the temperature of the device changes. Vanderbilt University scientists discovered this transition occurs at 68°C, much higher than room temperature. If the particle size is maintained at 10 nm or more, the temperature where the transition occurs can be lowered by as much as 35°C by adding small amounts of impurities to the vanadium dioxide. This sensor could be used to indicate critical temperatures in manufacturing environments. It could be made into a “solar shade” that automatically converts to reflecting mode when the temperature rises. Nanosensors could also be created that measure the temperature at different locations in human cells. This transition will find applications in “ultrafast” optical switches that could increase the rate of signal transmission in both optical communication and computing devices.

The use to which nanoscale sensors could be put is limited only by imagination, knowledge of the chemical and physical properties of nanodevices, and how clever we are at manipulating them. It is entirely reasonable to expect that nanoscale devices could provide sensors for any hazardous situation imaginable. Nanosensors could be used in roadways to indicate the presence of black ice, in bridges to provide early warning of structural failures, and in industrial environments to indicate the presence of dangerous levels of solvents, dusts, or other contaminants, thereby reducing the danger of accidental explosions.

FOR GREATER UNDERSTANDING

Questions

1. What does a sensor do?
2. What are some advantages of nanoscale sensors over macroscale sensors?
3. What is transduction?
4. What is one way in which nanoscale sensors provide transduction of their signals?

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2. The NASA *Science News* website features an article entitled "Electronic Nose" that provides details about possible uses for nanoscale sensors in space programs. — http://science.nasa.gov/science-news/science-at-nasa/2004/06oct_enose
3. The *Epoch Times* website provides an article entitled "Pancreatic Cancer Targeted by Nanotechnology," by Mimi Li from November 1, 2010. — <http://www.theepochtimes.com/n2/content/view/45192>

Lecture 10

Nanotechnology and Medicine

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 8: "Biomedical Applications."

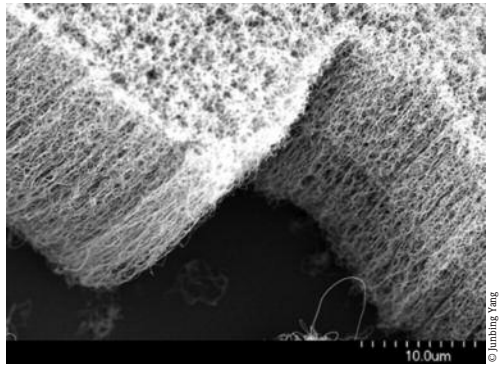
Nanotechnology is impacting every aspect of medicine, from diagnosis to treatment. Diabetics depend on regular testing to monitor and control their blood glucose levels. The decreasing size and increasing speed and sensitivity of glucose-testing devices over the past thirty years have improved the quality of life for diabetics substantially.

Nanotechnology promises to advance the science of glucose testing to an ultimate limit. Recently, scientists at Purdue University reported the design of

a precise biosensor for detecting blood glucose using hollow structures called single-walled carbon nanotubes anchored to gold-coated "nanocubes."

The device resembles a tiny cube-shaped tetherball. The end of the tetherball is the gold sensor. The rope holding the tetherball is a carbon nanotube. The nanotube is composed of carbon atoms and is about 2 nm in diameter. It acts simultaneously as the tether and as an ultrathin wire to conduct electrical signals, according to Timothy Fisher, a Purdue University professor of mechanical engineering. As of 2009, the device detects glucose more precisely than any other biosensor.

The tetherball design is a breakthrough in sensing technology. It allows the sensing portion of the system to extend from the device. This should allow the business end of the sensor to more easily come into contact with its target molecules. The tether means that the sensor is not dependent on diffusion to bring the target molecules in contact with it. The tether can also allow the sensor to move to other regions to enhance sensing. This tethered nanodevice provides a substantial improvement in sensitivity over existing devices, reducing the concentration of glucose required to stimulate a response by a factor of five. The new sensor also can operate over a wider range of glucose concentrations, which means it could be used for



A scanning electron microscope view of aligned single-walled carbon nanotubes (SWNTs) from a controlled growth experiment in 2005.

many purposes. Most sensors can either sense small quantities or detect a wide range of concentrations. Very few sensors can do both.

Pancreatic cancer has a devastatingly low survival rate, causing more than 35,000 deaths in the United States every year. The primary reason for the high fatality rate (less than 5 percent of patients survive five years after diagnosis) is because pancreatic cancer is difficult to diagnose and is usually only identified at an advanced stage. Nanotechnology techniques are being examined both as potential early-warning sensors for pancreatic cancer and as avenues for delivering targeted treatment.

In 2009, researchers at Emory University led by Lily Yang, M.D., Hui Mao, Ph.D., and Shuming Nie, Ph.D., reported a method for creating nanoscale sensors that allow early diagnosis of pancreatic cancer. The sensors consist of iron oxide nanoparticles, which have a core that is 10 nm in diameter, and are coated with an engineered biomolecule that binds specifically to pancreatic cancer cells. The nanoparticles aggregate on the cancer cells and are clearly visible using standard magnetic resonance imaging (MRI). These sensors have been tested in mice with implanted human tumors. The sensors have another advantage; they can be studded with near-infrared dye molecules and then seen by scanning the mice with an infrared camera. In addition, the method has the advantage of distinguishing cancer cells from those associated with chronic pancreatitis. The properties of the nanoparticles are described in "Molecular imaging of pancreatic cancer in an animal model using targeting multifunctional nanoparticles," published in the journal *Gastroenterology*. Dr. Nie is the principal investigator, and Dr. Yang is a member of the Emory-Georgia Tech Nanotechnology Center for Personalized and Predictive Oncology.

Researchers at Rice University's Laboratory for Nanophotonics (LANP), Baylor College of Medicine's Radiology Department, and the University of Texas's MD Anderson Cancer Center are taking nanosensors one step further by examining the role of gold-coated nanoparticles in identifying and treating pancreatic cancer. Their approach, which they have named "theranostics," uses nanoscale sensors to simultaneously diagnose and treat pancreatic and other cancers. The nanoparticles they are examining bind preferentially to cancer cells. In addition, the particles include a gold nanoshell that converts infrared light into heat to kill cancer cells. For the most part, infrared light passes harmlessly through the human body. However, modifying nanoparticles by coating them with an infrared sensitive dye allows the nanoparticles to selectively absorb the radiation. The particles can convert the optical energy and release it locally in the form of heat sufficient to kill adjacent, cancerous cells. The dye can also be optimized to make the tumors obvious in either optical and MRI scans for diagnosis.

Unfortunately, many pharmaceutical compounds have low solubility in water. This makes it difficult to administer them intravenously because they

can precipitate or clump in the blood stream. A number of different approaches have been studied to improve the solubility of effective drugs.

One is called “nanoencapsulation.” It uses a commonly available technique, ultrasonic irradiation, to separate the drug molecules from one another. Each small piece of drug then gets coated with naturally occurring sugars—polysaccharides—which are very soluble in water. The sugar encapsulation improves the water solubility of the drug without adversely affecting its effectiveness and is stable enough to prevent the drugs from reprecipitating in aqueous environments.

In a more chemically intensive approach to the solubility problem, both synthetic and naturally occurring nanoparticles have been studied for use as protective carriers for pharmaceutical compounds. When properly engineered, nanostructures can control and sustain the release of medicines. A variety of methods for preparing nanoparticles encapsulating drugs have been developed. Some involve polymerization reactions and some involve self-assembly, where the natural attractions between components are manipulated to form a protective environment around the drug.

Photodynamic therapy is used in a variety of cancer treatments. It depends on selective delivery of a photosensitizer to cancer cells. The photosensitizer is a molecule that absorbs wavelengths of light generally transmitted by healthy tissue. Nanotechnology can improve photodynamic therapy by encapsulating the photosensitizer and coating it with proteins that specifically bind to the surface of cancer cells. Absorption of light then provides local heating or produces a particularly toxic form of oxygen called singlet oxygen, in the immediate environment of a cancer cell. The localization increases toxicity to cancer cells and reduces toxicity to healthy cells when compared to standard chemotherapy or radiation approaches. The approach works best for tumors within a few centimeters of the surface of the skin, because that is as far as light penetrates into the skin.

Biologists have long recognized that sharks are unique among sea creatures in that algae do not grow on their skin. It appears that shark skin resists algae colonization because of its physical structure, not its chemical properties. Scanning electron microscopy revealed the physical structure of shark skin. Now, an engineered material called Sharklet™ is the world’s first synthetic product demonstrated to inhibit bacterial growth through surface pattern alone. The Sharklet™ surface comprises millions of tiny diamonds arranged in a distinct pattern on a plastic substrate. The roughness of the surface mimics the width-to-height ratios that appear responsible for the microbe-resistant properties of shark skin. Sharklet Technologies puts the pattern into adhesive-backed plastic films and manufactures the pattern into medical devices and consumer goods to prevent bacteria growth. Sharklet™ has been shown to be a simple, cost-effective solution for bacteria control.

Nanotechnology has recently been applied to the problem of developing sensitivity in artificial skin. Researchers at the University of California, Berkeley, have developed nanowire arrays that work at the low-voltages needed to make flexible and responsive artificial skin. The researchers made the circuit arrays by growing nanowires on a silicon substrate and transferring them to a flexible “receiver” substrate by contact printing. The nanowires are mounted on a drum and then rolled across the receiver substrate, producing parallel arrays of printed nanowires. The process is quite similar to an old-fashioned printing press. The goal, ultimately, is to completely cover a robot body with electrically conductive “skin.”

Other researchers are focused on improving the success of bone grafts using nanotechniques. Nanoscale materials are clearly superior to standard macroscale devices in their physical properties and biocompatibility. They may improve osseointegration, which is crucial for long-term implant efficacy. Nanoscale analysis of implant surface quality also reveals that titanium surfaces that are rough on a nanoscale and coated with nanocrystalline hydroxyapatite in a protein matrix substantially improve ligament regeneration to an implant when compared to nanoscale smooth surfaces.

Spinal cord injury (SCI) can cause devastating disabilities. It has been realized for some time that rapid medical intervention is key to providing the best possible chance for recovery from traumatic SCI. Scientists at Purdue University have reported successful treatment of rats whose axonal membranes are injured by compression. The treatment is through prompt injection of 60-nm-diameter self-assembled micelles of a specific copolymer. Micelles injected intravenously allowed injured rats to recover locomotor function and reduced the volume and inflammatory response at the injury site. The nanomaterials appeared to be beneficial because they restored normal action potential along spinal nerves. Even more promising is that the micelles did not cause any adverse side effects in live rats.

Nano- or molecular motors occur naturally and play important roles in the normal functioning of the human body. Molecular motors are assemblies or proteins that use energy to actively intervene and move specific molecules around in cells and throughout organs. The sodium/potassium pump that restores charge balance after muscle contraction is a rotary-style motor that has inspired a variety of synthetic analogs. The kinesin motor that carries molecular cargo through cells like a nanoscale train moves because of a cyclical series of conformational changes. These are only two examples of the molecular motors at work right now in your body. Physicians are interested in developing synthetic nanorobots that could be powered by the body itself and deployed to repair damaged areas from inside the body or used to clean plaque from arteries.

Chemists have synthesized a number of different nanostructures that have been observed to move over surfaces under the influence of thermal motion

in those surfaces. But controlling the motion and action of nanomachines will take a more sophisticated approach. Two recent developments have occurred in this arena.

The first allowed chemists to observe some simple synthetic molecular machines called rotaxanes. These molecules are physically interlocked structures that consist of a dumbbell-shaped molecule whose rod section is encircled by a ring. The ring portion of the rotaxanes can be moved along the length of the rod by exposure to specific chemicals, light, or exposure to acidic compounds. The motion of these compounds on surfaces can be observed using STM. A thorough understanding of the mechanisms by which rotaxanes function will open doors to the development of more sophisticated molecular machines.

The second is the announcement of molecular spiders that can walk along DNA. The spiders are built of a streptavidin molecule and three deoxyribozymes as catalytic “legs.” They show simple robotic behavior when deposited on a surface coated with DNA. Using single-molecule microscopy researchers confirmed that these spiders were able to “walk” along a predetermined path and follow simple instructions embedded in the path. Specific amino acids on the DNA instructed the spiders to “start,” “follow,” “turn,” and “stop.”

Theoretical studies of the hydrodynamics of molecular machines that undergo regular cyclic conformational changes as a result of ligand binding and release have also been reported. When these changes occur in a fluid environment, complementary changes occur in the solvent surrounding the machine. These changes allow the molecular machine to move through the fluid, much like a human can swim through water.

Nanotechnology holds hope for those suffering from neurodegenerative diseases such as MS or ALS, or those caused with traumatic nerve damage. Efforts to construct neuro-electronic interfaces that would permit external computational devices to replace defective nerve transmission lines are underway. The challenges are perhaps more substantial than those faced by drug developers or nanomachine builders. Nerve transmission occurs at speeds associated with quantum tunneling and is controlled by rapid variations in the concentrations of sodium and potassium ions along the nerve. Nano-nerve interfaces will need to be constructed of biocompatible materials, as will all of the medical nanomachines discussed here. But nerve interfaces will need to respond at rates not currently accessible by today’s computers.

FOR GREATER UNDERSTANDING

Questions

1. Why is nanotechnology of such intense interest to medical researchers?
2. What is encapsulation?
3. How does photodynamic therapy work?
4. What are some natural molecular motors? How sophisticated are nanomachines today?
5. What particular challenge is faced by doctors who want to use neuro-electronic interfaces to treat neurological disease?

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1. The *Purdue University News* website features an article from January 2009 entitled "Nano-tetherball Biosensor Precisely Detects Glucose." — <http://news.uns.purdue.edu/x/2009a/090122FisherBiosensor.html>
2. Professor Aristides Requicha, founder of the Laboratory for Molecular Robotics at the University of Southern California in Los Angeles, provides an article entitled "Nanorobotics." — <http://www-lmr.usc.edu/~lmr/publications/nanorobotics>

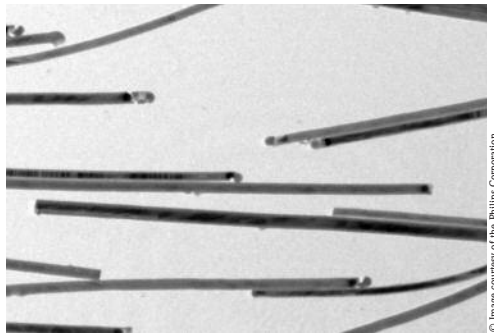
Lecture 11

Nanotechnology, Optics, and Electronics

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 9: "Optics and Electronics."

The most obvious applications of nanotechnology are probably in the world of electronics and computing. Recall that Gordon Moore, a cofounder of Intel Corporation, predicted that the amount of space required to install a transistor chip would drop by half every eighteen months. The prediction is called Moore's first law. A corollary, Moore's second law, says the cost of building a factory to make those chips doubles every three years. Obviously neither law can continue forever. However, over the past forty-five years, Intel and their competitors have kept up the pace predicted by Moore when he first stated his laws in 1965. As a result, today consumers get more functions on an integrated circuit chip at a significantly lower cost per function than in 1965. As a result, everything from your car to the least expensive kid's toy includes computers. Over the past fifty years, computer technology has revolutionized life. There is every indication that over the next fifty years, this trend will continue.

Since the advent of the transistor, computer manufacturers have been committed to increasing the amount of data that can be stored in a given space and the rate at which computations could be performed. Both depend directly on the size of the components of an integrated circuit—transistors and other components. A transistor is a device used to amplify and switch electronic signals. It is composed of semiconductor material, a material that is normally nonconducting, but which can easily be converted to a conductor by application of an external voltage or current. A transistor has three or more terminals that allow it to connect to external circuits. Transistors can act as both amplifiers and as switches.



NanoLEDs

Nanowires of indium phosphide (InP) are well suited for miniature light-emitting diodes (LEDs) in the yellow and green color range. The LED is obtained by introducing a junction between differently doped regions within a wire. NanoLEDs are promising for light-emitting displays, integrated optics for communications purposes, or light sources.

Simple electrical circuits are composed of conductors, mostly metals, that follow Ohm's law, $V = IR$ (voltage equals current times resistance). A variety of components can be included in traditional circuits to control or modify the voltage or current flowing through the circuit. These include resistors, capacitors, and inductors. All can be made of metal wires arranged in appropriate structures. In traditional circuits, electrons move under the driving force provided by the voltage, causing a current. Transistors, in contrast, are composed of semiconductor materials, including silicon, germanium, gallium, and other elements. They can also be controlled by applying voltage to modify the current flowing through the device. But they don't always follow Ohm's law. Semiconductors come in two types, N-type, where electrons provide the charge carriers, and P-type, where the absence of electrons, called holes, provides the charge carriers. Unlike metals, which are always conductive, semiconductors only conduct electrical signals under the right set of voltage conditions. Integrated circuits (IC) include transistors, resistors, diodes, and capacitors in one integrated device to allow control of precise electrical signals. Modern methods of producing integrated circuits use lithographic techniques. The methods have been refined and are so efficient that the cost of integrated circuits is lower than ever, despite Moore's second law.

The history of integrated circuits is one of miniaturization.

Lithographic production of integrated circuits has supported the miniaturization of silicon devices for the past fifty years. It represents the ultimate refinement in top-down production techniques. But the fundamental laws of physics are already restricting our ability to continue miniaturizing computer components using lithography.

Smaller circuit features allow higher information density and faster computational turnover. Today, chips are being built with 32 nm features. Soon the physical limits of semiconductor circuits will be reached. It will be impossible to reliably store charges in the area allocated for memory, or to keep the charges in one component of the IC from interfering with charges in an adjacent component. They will simply be too small to operate independently. Quantum mechanics will allow charges to leak from the quantum scale features in the semiconductors. At this point, the integrated circuit will have to enter a new era, the era where molecules rather than semiconductor materials will be required to make circuit components.

Among the molecules being investigated for use in molecular computers are carbon nanotubes, as well as traditional organic and organo-metallic molecules. Depending on their structure, carbon nanotubes can behave like either semiconductor or metallic materials, or even as transistors. Despite these properties, there are significant challenges to building circuits using nanotubes. Nanotubes are sticky and more difficult to control than molecules of similar size. Molecules have inherent variations in electron density, which makes it possible to use intermolecular forces to

attract and control them. Nanotubes are uniformly attracted to each other, making it more difficult to find a tool to move them. Nanotubes can have different configurations, and each configuration has different electrical characteristics. Large molecules are also inherently nanoscale devices. Over the past ten years scientists have demonstrated that there are single molecules that can act as switches and can behave like superconductors and transmit current without loss. This makes molecular circuits an attractive area of research, although they have yet to be demonstrated in commercial applications.

The densest memory storage today depends on the magnetic properties of nanosize chunks of materials. The magnetic features of modern memory devices store information in a binary format—the magnetic regions are polarized in one of two ways—think of it as 1 or 0 or as a compass needle that can only point north or south. However, to be stable, magnetism requires cooperation among a set of atoms. If the size of the features in a magnetic storage device becomes too small, then the normal thermal motion of the device becomes sufficient to interfere with the long time stability of the magnetic polarization. To increase the density of information storage past this point, alternate methods of storing information must be found.

One proposal for continuing to increase the density of information storage is to move from the essentially two-dimensional world of integrated circuits to a truly three-dimensional environment. To achieve three-dimensional information storage, we need to move into the optical realm. Three-dimensional storage of information can be secured using holographic techniques. Holograms are images created by interference between two components split from a single laser beam. Holographic memory will provide faster access than magnetic or optical disks. Instead of providing a sequential feed of bits of information, holographic storage will allow all the information to be delivered simultaneously. Some researchers believe that a holographic data storage system could accommodate thousands of pages (blocks of data), each containing millions of bits, in the volume of a sugar cube. This translates to a storage capacity of 10 Gb per cubic centimeter, reflecting two-dimensional magnetic storage densities of around 100 Kb per square centimeter.

At this density, a terabyte of data could be stored in a block of optical media about the size of a deck of playing cards. In contrast to today's data storage, optical systems will not have any moving parts. They will allow all the "pages" to be accessed simultaneously rather than sequentially. These two characteristics mean that it will be possible for optical data storage devices to operate at 1 gigabit per second (Gbps) or faster. Iron-doped lithium niobate is the medium being investigated for holographic data storage systems. It is the only material now known to have the uniform optical quality required to support holographic memory. But it also has several shortcomings that will need to be overcome to make it commercially useful.

A prototype molecular memory system has been constructed using the protein bacteriorhodopsin embedded in a polyacrylamide gel. The protein gets fixed in a specific conformation by the polymerization of the gel. A set of krypton lasers and a charge-injection device (CID) array surround the cuvette holding the sample and are used to write and read the data. The bacteriorhodopsin molecule has the advantage that it changes states within microseconds. But given the several steps required to read or write a data bit, it takes about 10 milliseconds to access information in bacteriorhodopsin today. However, like the holographic storage, this device obtains data pages in parallel, so a net speed of 10 Mbps is possible. This speed is similar to that of slow semiconductor memory today. Nevertheless, the advantages inherent in three-dimensional data storage continue to motivate research into design and development of molecular storage media.

As we have already discussed, nanoscale materials can often have properties that differ significantly from the same materials when they are in bulk samples. Even though nanostructured and nanoengineered products are appearing in the marketplace, we still don't understand how to control or modify the properties of nanomaterials. In traditional conductors or semiconductors, *vacancies* (also called *Schottky defect*) play a major role in determining the electrical conductivity and thermal properties of the material. Often mechanical properties are affected, too. Vacancies reduce the hardness and the melting point of bulk materials. A vacancy is simply a site that should be occupied by an atom, according to the regularity of the three-dimensional lattice structure of a solid, but is not. The effect of the size of nanomaterials on the thermodynamics of vacancy formation has been investigated theoretically. The results predict that the vacancy concentration in a nanomaterial increases as the size of the material gets smaller, and increases as the temperature increases. This result is important because it helps to understand how the mechanical, electrical, and thermal properties are modified at the nanoscale. Under normal conditions, the calculation predicts that nanomaterials should suffer less than one vacancy per one million atoms. This explains why nanomaterials appear to be perfect: they contain fewer than 10^6 atoms and are therefore unlikely to contain a vacancy.

But not all researchers are committed to making current computer technology smaller and faster. Some believe that computing, in fact, is rapidly moving away from traditional computers. They expect that in the future, computer programs will not run on a desktop or even a handheld device, but will run on collections of mobile processors that will communicate over ad hoc networks. They call these collections "swarms." They predict that computational swarms will be governed by the same rules that govern natural swarms, like beehives or ant colonies. The collective behavior of the individual members will determine the behavior of the swarm. They are interested in studying swarm behavior and examining how it will affect computing.

Any practical application of swarm computing lies in the future. However, there is already evidence of a massive shift from personal desktop computers to mobile network-enabled devices (for instance, smart phones and tablets). And despite its relatively short history, computing has already gone through one rapid revolution: the switch from massive mainframe to personal computers. The conversion from PCs to the swarm should be expected to be at least as rapid as the last shift in the twentieth century. Theoretical models are being used to examine and explain the behavior of swarms and harness their strengths to rationally optimize the technology shift as it moves forward.

Another shift already underway is the shift from local storage of information to the “cloud.” Cloud computing relies on remote storage of data and software and is dependent on the Internet for access to both the information and computational space. As wireless devices become ubiquitous and more powerful, the use of the cloud, which guarantees access to all your information at any time from any place, becomes more and more attractive.

Another application of continually improving electronic devices lies in the area of photovoltaics. The same semiconductor material that is used to build integrated circuits can be used to convert sunlight directly to electricity. In an era of global warming and peak oil production, many believe that the future of our energy-dependent society depends on our ability to efficiently convert solar energy into more useful forms.

Efforts to improve the efficiency with which electricity is produced in solar cells look to nature for inspiration. Nature uses photosynthesis to power all life. It is no exaggeration to say that our current petroleum-powered economy is ultimately derived from photosynthesis. In mimicking photosynthesis, scientists have tried to improve the efficiency of collection of photons by adding molecular antennas that efficiently absorb them, providing a reaction center that allows a substantial separation between the electron produced by the photon and the hole it leaves behind, and a membrane designed to convert the electrical energy and store it until it is needed. The molecules that play a role in photosynthesis are nanoscale. So it makes sense that we try to improve the conversion of solar energy using nanoscale structures. Ideally, we would want to use a blackbody absorber to capture all the solar photons, hook this up to a molecule that could produce a large-distance charge separation in response to the excitation caused by the photon absorption, and an ideal battery to store the energy until we need it. Today’s best solar cells use organic dye molecules to improve the absorption of photons. The dye molecules are attached to a titanium dioxide semiconductor that produces an efficient charge separation. And the energy is used to drive a reversible chemical reaction, which charges a rechargeable battery. The battery stores the power until it is needed.

One specific technological improvement in light emitting diodes (LEDs) is bringing a whole new generation of efficient light sources to market. LEDs are just photovoltaics run in reverse. Instead of absorbing photons and producing electricity, they consume electricity and very efficiently produce photons. LEDs have been around since about 1960. The energy gap of the semiconductor determined the color of light that was emitted. Eventually, scientists determined a method for coating a phosphor on an indium gallium chip that produced blue light. The phosphor shifted the wavelength of the emitted light, producing the entire range of visible wavelengths and creating white light from a single diode. The low cost of semiconductors means that they produce more light for a given amount of money than any other commercially available light source.

Other studies are underway to scavenge waste or byproduct energy to power a variety of low-current devices. Some of these efforts focus on optimizing the use of piezoelectric materials. Piezoelectric materials produce a voltage when they are mechanically deformed. Traditional piezoelectric materials are crystalline or ceramic in structure. So, though it might be tempting to simply use piezoelectrics as the soles of your shoes and deform them with every step, that arrangement is not very comfortable. Recent synthetic efforts have produced nanometer-thick piezoelectric crystals embedded in flexible plastic, which would work well as shoe soles. Although detailed studies on the utility of the devices have not been conducted, the idea that waste energy can be scavenged and used to power a variety of devices is sufficiently appealing that it continues to attract research interest.

Modern communications use technologies at the interface between optics and electronics. Optical fibers carry information efficiently and at much higher densities than traditional electrical cables, or antenna-based systems. Much of this density and efficiency is attributable to the fact that photons do not have charge or mass. They are therefore much less likely to interact with each other than electrons are. Using a variety of wavelengths of light, or a variety of polarizations, or a variety of pulse rates can all allow multiple streams of information to be simultaneously transmitted on a single fiber-optic cable. This simultaneous transmission of information is called multiplexing. Photons are also much less likely to produce heat as a byproduct of their interactions with the medium through which they are being propagated than electrons in electrical components are. Nanotechnology has played an important role in improving fiber optics. Modern fiber optics can be doped with nanostructures that support more complete polarization of light, for instance, allowing better multiplexing. But eventually, signals transmitted through fiber-optic cables still need to be converted to electrical signals in semiconductor material devices in order to be transduced into signals we can understand. The optical revolution is not yet complete.

FOR GREATER UNDERSTANDING

Questions

1. Why are optical media able to store information at a higher density than electronic media?
2. How are solar cells related to light emitting diodes (LEDs)?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

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2. The University of Virginia Department of Computer Science provides an introduction to swarm computing with links to articles and other websites. — <http://swarm.cs.virginia.edu>
3. The *Ars Technica.com* website features an article by Casey Johnston entitled “Piezo-rubber Creates Potential for Wearable Energy System.” — <http://arstechnica.com/science/news/2010/03/piezo-rubber-creates-potential-for-wearable-energy-system.ars>
4. The *National Geographic News* website provides an article by Stefan Lovgren from 2005 entitled “Spray-On Solar-Power Cells Are True Breakthrough.” — http://news.nationalgeographic.com/news/2005/01/0114_050114_solarplastic.html
5. The *Nanotechnology Now* website provides an article by Lance Mudryk from May 2010 entitled “Prof Researching Better Solar Panels.” — http://www.nanotech-now.com/news.cgi?story_id=38237

Lecture 12

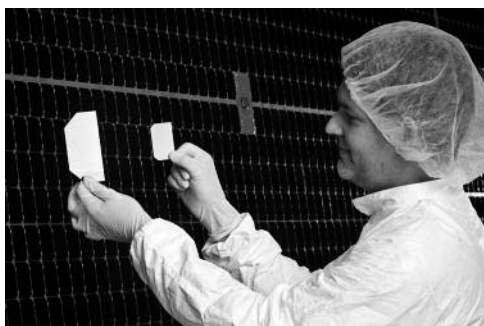
Nanotechnology and Energy

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 5: "Points and Places of Interest: The Grand Tour."

Those cognizant of the current costs of obtaining, transporting, refining, and utilizing petroleum as our primary energy source are looking at nanotechnology for potential solutions to the growing problem of energy.

To many, the holy grail of the energy domain would be to efficiently capture, store, transmit, and utilize solar energy. In use, solar is potentially a very clean method of energy generation. The total solar energy absorbed by Earth's atmosphere, oceans, and land masses is approximately 3.850×10^{21} joules per year. In 2002, the Sun provided more energy in one hour than the world used in one year. Of course, the world's energy consumption is skyrocketing. The U.S. Energy Information Administration projects that annual world energy consumption will double by about 2035. Then the world will be consuming the equivalent of two hours of sunlight per year. There are 8,760 hours in a year. We need $(2/8,760) \times 100 = 0.023$ percent of the Earth's surface covered with 100 percent efficient solar arrays to provide this energy. The surface area of the Earth is 5.16×10^8 square kilometers. By this calculation, we would need to cover about 120,000 sq. km with 100 percent efficient solar cells that would be illuminated twenty-four hours a day to support the Earth's demands. The area required is about the size of the state of Pennsylvania. Of course, anything less than 100 percent efficiency means we need to cover more than one state's worth of area. And no place on Earth has access to twenty-four-hour solar illumination.

How efficient are today's solar cells? Boeing's subsidiary Spectrolab claims production of commercially available solar cells with 39.2 percent efficiency in the early 2010s. These cells are not likely to be available to you at your local home store in the immediate future,



© Image courtesy of The Boeing Company

In 2009, Spectrolab set a new world record in terrestrial concentrator solar efficiency with a triple-junction, lattice-matched solar cell that converts 41.6 percent of sunlight into electricity. Spectrolab forecasts producing about 150 megawatts of solar cells to its photovoltaic customers in 2011.

however. They were developed for use in satellites, where other sources of power are even more prohibitively expensive than solar. The high manufacturing costs of these cells limits them to being economically viable in only the most advanced and demanding environments.

Of course, many technologists are banking on applications of nanotechnology to reduce costs and improve efficiency so that solar cells become more attractive as energy sources in the future. Today, solar cells are photovoltaic cells generally made of silicon semiconductor material. They work by absorbing photons of light and converting the energy to knock electrons out of their minimum energy locations and into a conduction band. Electrons in the conduction band can flow, forming a current that we identify as electricity. The drawbacks of silicon solar cells lie in their fundamental physics. First, lots of the photons from the sun are too low in energy to kick electrons out of their minimum energy environments. Others have too much energy. In addition to kicking electrons into the conduction band, their extra energy gets degraded to heat. These phenomena reduce the theoretical efficiency of silicon photovoltaics to about 30 percent. That is, about 30 percent of the photons that hit the solar cell will be of the correct energy to generate electricity. Current mass-production techniques, while having the advantage of reducing the cost of photovoltaics, do so at the expense of solar-conversion efficiency. The efficiency of the solar cells that can be bought at a home store today is around 10 percent. That means only 10 of every 100 photons that hit the surface of the solar cell actually get converted into electricity.

Since 2001, chemists have designed several strategies for increasing the efficiency and reducing the cost of solar cells. One strategy is to make solar cells out of plastic. Plastic substrates reduce the cost of solar cells because silicon semiconductors are manufactured in expensive clean rooms. Research labs make plastic solar cells starting with the raw materials in a beaker on the lab bench. This is a much less intensive manufacturing approach. Chemists at the University of California in Berkeley have made plastic solar cells that utilize carbon nanorods dispersed in a plastic substrate as both absorbers to convert solar energy to electricity and as wires to carry the energy to external connectors.

Konarka Technologies manufactures a product called “Power Plastic.” Power Plastic absorbs sunlight or indoor light and converts either into electricity. Their technology is secret, but basically, Power Plastic is made by embedding nanoscale titanium dioxide particles coated in photovoltaic dyes in plastic. The dyes act to extend the limits of the electromagnetic spectrum that are absorbed by the nanotitanium dioxide, increasing the efficiency to around 8 percent.

Fujitsu Labs reports a hybrid device that harvests energy to generate electricity from both heat and light. The technology was first reported in 2010. The device overcomes one complaint about energy harvesting—it is very inefficient. Harvesting devices produce only a fraction of the power that

batteries can. A single device that can capture energy from both light and heat ameliorates the efficiency problem by utilizing two different inputs. The device connects two types of semiconductor materials (P-type and N-type) to function as both a photovoltaic cell and a thermoelectric generator. An alternate version can be manufactured from inexpensive organic materials, helping to keep production costs low. One application could be in medicine, where the sensors could monitor conditions such as body temperature, blood pressure, and heart rate without supplemental batteries or electrical wiring. The dual energy sources, light and heat, would provide the sensor sufficient energy to operate. Another application might be in remote area environmental sensing for weather forecasting or atmospheric monitoring. Even if it were not possible to replace batteries on a regular basis, or if power lines were not available, the sensor could draw its power from ambient heat and light. These devices are still under development, but they are expected to be commercially available around 2015.

As we attempt to improve the efficiencies of solar cells and power generation, can we harness the promise of nanotechnology to work on the other side of the equation and reduce our consumption of power instead? Probably the most obvious way in which nanotechnology will affect our power consumption is through the use of light emitting diodes (LEDs) to replace traditional incandescent and fluorescent bulbs as light sources in our homes, offices, and elsewhere. Traditional incandescent bulbs have changed little since they were invented by Thomas Edison in 1879. Though they provided a substantial improvement over candle, kerosene, oil, or gas lights in the nineteenth century, they are some of the energy pigs of the twenty-first century. You probably know from firsthand experience that incandescent bulbs produce significant amounts of heat, in addition to light. The heat is a waste product if you are using the bulb as a light source. The light is a waste product if you are using the bulb as a heat source. Typical incandescent bulbs are no more than 20 percent efficient. Modern technology is producing new lighting devices that substantially improve this. In fact, the Energy Independence and Security Act of 2007 determined that incandescent light bulbs will not be sold in the U.S. after 2014. The first wave of high-efficiency lighting is being implemented using compact fluorescent and halogen bulbs, but LEDs are by far the most efficient option. Lighting accounts for about 15 percent of the electrical use in a home, so tripling the efficiency of lighting promises a substantial positive impact.

The LED revolution has been made possible by a series of technical improvements over the years. Until recently, LEDs were used as single indicator lights in instrument panels, electronics, and pen lights. "Clustering" the small bulbs together allowed an expansion of their application. Clustered bulbs were first used in battery-powered items such as flashlights and headlamps. Today, LED bulbs are made using as many as 180 bulbs per cluster and encased in diffuser lenses that spread the light in wider beams.

They are available with standard bases that fit common household light fixtures, bringing LEDs to home lighting.

The high cost of producing LEDs has been a roadblock to widespread use. LEDs were originally made on sapphire substrates. Today, silicon wafers can replace the sapphire, substantially reducing LED costs. There are a number of benefits in using LED light bulbs, which offset the high manufacturing cost. LEDs last much longer than typical incandescents, produce much less heat, are mercury free, and are more efficient in converting electricity into light than other lighting options. They are better suited to being powered by solar panels because of low power requirements. Generally, LED lighting uses one-third the energy of incandescent bulbs.

Since the mid-2000s, researchers have looked to organic materials as possible substitutes for traditional semiconductor materials as LED substrates. Organic light emitting diodes (OLEDs) are lower in cost and promise flexibility that is not possible in crystalline semiconductors. Carbon nanotubes have the advantages of being both highly conductive and quite flexible and have found application in OLED formulations. Thin sheets of carbon nanotubes can be made using technology remarkably similar to that used in manufacturing paper. These sheets are conductive and flexible, with the additional advantage of being thin enough to be transparent. All of these properties make carbon nanotubes attractive components for the next generation of organic LEDs.

Other applications of nanotechnology may improve the efficiency of fuel cells. A fuel cell converts a fuel, most promisingly hydrogen, into electricity, via an electrochemical process. It is similar to a battery, but it is not a sealed device. Like batteries, fuel cells have two electrodes, an anode and a cathode. In a fuel cell an electrolyte lies between the electrodes. Hydrogen, or a hydrogen-containing fuel, is fed into the anode. A catalyst at the anode facilitates ionization of the hydrogen atoms. The protons pass through a selective membrane, while the electrons travel on an external path, creating a usable electric current just like batteries do. The protons and electrons are reunited at the cathode, where the hydrogen reacts with oxygen from the air, forming water.

In contrast to engines that extract energy from fuels by combustion, fuel cells are more efficient, less polluting, and quieter. If hydrogen is used as the fuel, the fuel cell produces only water and electrical energy. Hydrogen fuel cells will eventually provide a better source of energy than solar conversion, because they would not require that we cover large areas with solar cells. If we can figure out how to efficiently produce it from water, hydrogen could provide an essentially limitless, non-polluting source of energy. However, hydrogen is a hazardous and highly energetic material that poses specific risks in generation, transport, and storage.

Today, fuel cells running on methanol and improved through nanotechnology are commercially available. A German company, Smart Fuel Cell AG, sells

methanol fuel cells that provide 600 to 16,000 watts per day of power. They have substantially reduced both the size and cost of their fuel cells by using nanoparticle catalysts and replacing standard polymeric electrode assemblies with specifically nanostructured three-dimensional membrane electrode assemblies (MEA). The nanoparticle catalysts formulation enhances the surface area available to support hydrogen ionization. The higher surface area means that less catalyst is needed to support fuel cell operation. The reduction in size, mass, and cost of the fuel cell can be significant. Use of a nano-engineered membrane electrode assembly allowed Smart Fuels to improve the performance of their fuel cells by a factor of three, while reducing the weight of catalyst required by 75 percent.

A variety of nanoscale materials with potential utility as fuel cell catalysts have been reported over the past few years. Among them are novel 24-sided platinum nanoparticles that show up to four times greater catalytic activity compared with commercial catalysts. Made by material scientists at Georgia Technical Institute, arrays of vertically grown carbon nanotubes doped with nitrogen are much cheaper and longer lasting than the platinum catalysts currently in use developed at the University of Dayton and scientists at Institut National de la Recherche Scientifique (INRS) in Quebec. These nanotubes have generated an entirely new class of catalysts by using carbon black ammonia and iron acetate to synthesize a catalyst where nitrogen atoms bind across nanosized gaps in the carbon structure, forming active catalytic sites.

Nanoscale materials modeled on natural zeolites may provide safe storage for hydrogen by providing small caverns that can store individual hydrogen molecules separated from one another. When surrounded by an inert environment, hydrogen is much less likely to explode than when it is stored in a bulk container. Zeolites are naturally occurring crystals with complex, open, three-dimensional structures that make them ideally suited as absorbents. Zeolites at low temperatures can absorb a wide variety of gases and liquids. And frequently, just a small increase in temperature can result in the zeolites slowly releasing the absorbed materials. Scientists estimate that zeolites capable of absorbing 7 percent of their mass in hydrogen could provide a commercially viable hydrogen fuel tank for automobiles. Today zeolites are active ingredients in cat litter. Tomorrow, they may well serve as a hydrogen storage device in your car.

Lithium-ion batteries support today's electronic revolution. They power laptops, cell phones, MP3 players, digital cameras, and many other electronic products. Today, battery size is a primary factor limiting further miniaturization and performance improvements in many electronic devices. Nanotechnology is being investigated as a route to improve electrodes. Chinese scientists have prepared tin nanoparticles encapsulated in elastic hollow carbon spheres that show great potential for improving the operating voltages and lifetime of lithium-ion batteries. However, using tin in an

anode raises problems similar to those of building an automobile engine out of aluminum—it expands in use. Scientists in China report a resolution of this problem—they encapsulate tin nanoparticles in elastic, hollow carbon spheres. The elastic hollow carbon spheres act as a container, buffering the tin from damage associated with its volume variation.

Our current model of centralized power generation, accompanied by distribution through grids, provided a revolution for life in the twentieth century. However, grid distribution of electricity has inherent inefficiencies. Replacing the wire-based system with superconducting wires could improve power transmission efficiencies substantially. In metal wires like those in today's grid, resistance to current flow generates heat and reduces transmission efficiencies. Superconducting materials allow electrical conduction with essentially no resistance. The problem is that current superconductors operate only at low temperature, below 77°K, the boiling point of liquid nitrogen. Above this temperature, the thermal motion from the quantum behavior of solids disrupts the structure that supports superconduction in certain metal oxide solids. But we have seen that the properties of materials change when reduced to nanoscale. Scientists from the California Institute of Technology have created nanowire arrays that are superconducting at relatively high temperatures. The nanowires are made of a copper-oxide compound. Yttrium barium copper oxide (YBCO) is known as a high-temperature superconductor; it superconducts up to temperatures of 93°K, substantially above liquid nitrogen's temperature. The Cal Tech scientists fashioned YBCO strips into arrays of up to 400 nanowires each, aligned in parallel. Metal contacts run across the wires perpendicularly so that their electrical properties can be measured. Individual wires were as narrow as 10 nanometers and as long as 200 micrometers (millionths of a meter). The critical temperature, the temperature below which a material superconducts, was seen to vary with the wires' dimensions.

Another issue with grid distribution is with transmission efficiency. Transmission efficiency is improved by a reduction in the current. According to Joule's law, energy losses are directly proportional to the square of the current. Thus, reducing the current by a factor of 2 will lower the energy lost to conductor resistance by a factor of 4. Transmission and distribution losses in the United States are estimated at less than 6 percent when estimated from the discrepancy between energy produced (as reported by power plants) and energy sold to customers. Because superconductors offer essentially no resistance to electrical transmission, estimates are that transmission losses could be reduced by half, to 3 percent. The other 3 percent could be invested in keeping the transmission lines cold enough to maintain their superconducting behavior. Although not superconducting, the possibility of using carbon-nanotube-based transmission wires is also being investigated. Carbon nanotube wires could have significantly lower resistance than the wires currently used in the electric transmission grid.

FOR GREATER UNDERSTANDING

Questions

1. What is one major advantage of solar energy? What is one major drawback?
2. What advantage do OLEDs offer over standard LEDs?
3. What are the advantages of fuel cells? What characteristics of nanomaterials make them particularly useful in fuel cells?

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Zhang, Wei-Ming, et al. "Tin-Nanoparticles Encapsulated in Elastic Hollow Carbon Spheres for High-Performance Anode Material in Lithium-Ion Batteries." *Advanced Materials*, vol. 20, iss. 6, pp. 1160–1165. Weinheim, Germany: Wiley-VCH Verlag, 2008.

This article is available as a downloadable pdf from the Key Laboratory of Molecular Nanostructure and Nanotechnology at the Chinese Academy of Sciences, Institute of Chemistry ("Publications" tab). — <http://spm.iccas.ac.cn>

Websites of Interest

1. The NASA website features an article by Dr. Tony Phillips and Steve Price from 2006 entitled "Rocks in Your Gas Tank: Experiments Onboard the International Space Station Could Accelerate the Drive Toward a Hydrogen-Based Economy." — http://www.nasa.gov/vision/earth/everydaylife/apr_zeolite.html
2. The *EcoWorld* magazine website provides an article from 2006 entitled "How Much Solar Energy Hits the Earth?" — <http://www.ecoworld.com/energy-fuels/how-much-solar-energy-hits-earth.html>
3. The *Nanotechnology Now* website features an article by Richard Martel on organic LEDs from 2006 entitled "High Performance OLED on Carbon Nanotube Electrodes." — http://www.nanotech-now.com/news.cgi?story_id=15274

Lecture 13

Smart Materials

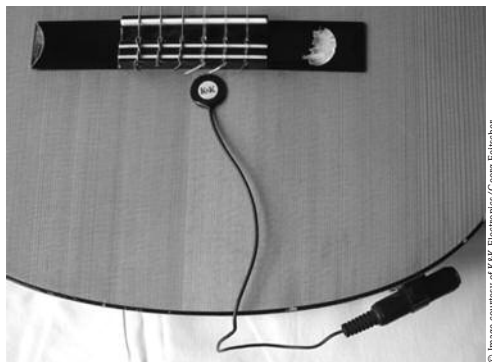
The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 6: "Smart Materials."

A smart material is a material designed to do a specific task or solve a specific problem or respond in a specific way to a specific stimulus. Mostly, "smart" materials are structures whose inherent properties can be chemically controlled to meet performance demands. Nanoscale smart materials take specific advantage of properties at the nanoscale that are different from properties at the macroscale. Smart materials should be efficient, keep us clean and disease free, or solve problems for us.

Nearly all of biology is composed of smart materials. Cell membranes are remarkable for their ability to recognize and transmit materials that need to move inside the cell while simultaneously denying entry to unnecessary or dangerous interlopers. In addition, they are to a large extent self-healing. Wouldn't it be great if we could design and manufacture consumer goods that shared this biological smartness?

Smart materials include piezoelectric materials, shape memory alloys, shape memory polymers, magnetostrictive materials, magnetic shape memory alloys, pH-sensitive polymers, non-Newtonian materials, photomechanical materials, and self-healing materials.

Smart piezoelectric materials are designed to bend, contract, or expand when a voltage is applied—or, conversely, to generate a voltage when mechanically deformed. In the former, piezo materials are used as precision positioning devices and are capable of acting as small mechanical switches. In the latter configuration, researchers are looking at ways to use piezoelectrics as energy scavengers that could convert the energy produced as a byproduct of normal activities (walking or bending your arm) into a source to power portable electronic devices and medical devices. The properties of piezoelectric materials have been shown to be size and shape dependent even when they are larger than nanoscale.



A piezoelectric disc used as an audio pickup on an acoustic guitar.

© Image courtesy of K&K Electronics/Greg Feltcher

This hasn't stopped a variety of improvements in creating piezoelectric devices over the past few years. Today, labs are creating piezoelectric materials that can be woven into clothing and used as simple logic gates. Engineers are examining the use of piezoelectrics for applications in environments where micro stresses can indicate future failure of joint, laminations, or other structural features.

Shape memory alloys and shape memory polymers can be set into a predetermined shape, usually by application of heat. They can then be reconfigured at low temperature and are metastable—they maintain the deformation—until you dunk them in hot water or expose them to body temperature, when they then spring back to their original configuration. The memory metal nitinol has a large range of applications, from the entertaining to the clever to the life saving. Nitinol has found commercial application as cell phone antennas that resist kinking and in extraordinarily flexible eyeglass frames that can recover even from the nastiest contortions. The most impressive use of nitinol is in medical applications, particularly for stents used by heart surgeons. Because of its superelastic properties, the nitinol stent can be compressed to the diameter of a wire to allow easy insertion in even the smallest arteries, and reliably returns to its initial expanded configuration when exposed to body temperature. The expanded stents hold arteries open, allowing blood to flow as it does in healthy arteries.

Nitinol is an alloy composed of about equal masses of nickel and titanium. As an entertainment, you can take a straight nitinol wire and bend it into any shape you like. It will stay in the shape you put it in indefinitely, until you drop it in a pot of hot water. Then it springs instantaneously, almost magically, back to its original, straight configuration. This is different from smoothing out a piece of wire you have bent, which remains wrinkled or retains stress points even after you smooth it out.

A phase transition, which occurs when the atoms in the alloy simply change their relative positions in three-dimensional space, is responsible for this extraordinary behavior. The two phases in nitinol are both solid phases, somewhat different from our normal experience with phase changes (of water, for example, which converts from solid ice to liquid water at 0°C).

In nitinol, as in a variety of alloy materials, the low-temperature phase is called martensite phase, and the high-temperature phase is called the austenite phase. Nitinol can be “trained” to always return to a specific condition by fixing its configuration and holding it there while it is heated to a temperature well above its martensite-austenite phase transition and slowly cooled. Once it has been cooled, it can be deformed into any other shape—the atoms will rearrange and maintain the new configuration—until you dip the material in hot water. The hot water provides sufficient energy for the nitinol sample to undergo the phase transition and rapidly return it exactly to its “trained” configuration.

Magnetostrictive materials are inherently “smart.” Composed of ferromagnetic elements including iron, cobalt, or nickel, magnetostrictive materials change their shape in response to an applied magnetic field. The shape change is due to the alignment of magnetic micro-structures in the samples, induced by the magnetic field. This is a completely reversible process; the material relaxes to its initial shape when the magnetic field is removed. Magnetostrictive materials can therefore be used as positioning devices. As in piezoelectrics, the magnetostrictive effect can be turned around—applying a mechanical stress can cause a change in the magnetic properties in the samples. The resulting time-changing magnetic field will induce a voltage that can be detected as a measure of the mechanical deformation. Interestingly, because magnetic alignment depends on the bulk properties of the materials, nanoscale grain structures can actually reduce the magnetostrictive response of samples.

Ferrofluids are some of the most impressive smart materials. Ferrofluids are colloidal mixtures of nanoscale ferromagnetic particles. Colloidal solutions are solutions that contain suspended particles from 5 and 200 nanometers in diameter. Homogenized milk is a colloidal suspension in which the milk fat is present as small colloids dispersed in a solution, primarily water. Solutions are mixtures of two or more compounds. The majority component, called the solvent, is in this case a liquid, water. The other components are solutes. Homogeneous solutions are formed when there are strong forces between the solvent molecules and the solutes so that the solutes stay dispersed in the solvent liquid at a molecular level. Solutions and colloids are historically differentiated by the way in which they interact with visible light. Light passes directly through a solution, unless it is specifically absorbed by one of the components. If you shine a laser pointer through a glass of water, the light travels through the water in a beam, which you can easily see in a dark room. However, if you shine a laser pointer through a glass of milk, you will observe that the laser light is scattered. The laser light exits the colloid like a cloud of light, coming from all directions, not a beam. Because the size of the nanoparticles is about the same as the wavelength of the light, the wave behavior of the light causes it to be scattered as it tries to travel through the milk. This scattering, called the Tyndall effect, is a traditional rule of thumb used to distinguish colloids from solutions.

Colloids can be formed when the solute does not have strong intermolecular interactions with the solvent. In milk, the nonpolar fat molecules prefer to be separate from the polar water molecules. And in nonhomogenized milk the cream rises to the top. The oil floats on the vinegar in salad dressing for the same reason.

In ferrofluids, the iron-containing components would normally separate from the liquid. But, both because of their small size and because of the presence of surfactants, the ferrofluids can remain a solution indefinitely.

Surfactants are molecular mediators. One end of a surfactant is nonpolar; the other end is either polar or charged. The nonpolar end is attracted to the nonpolar component in a solution; the polar end is attracted to the polar component. The surfactants surround the solutes and mediate their interactions with the solvent. The solute-surfactant-solvent interactions are strong enough to keep the solute dispersed indefinitely in a colloid.

Ferrofluids become strongly magnetically polarized in the presence of an external magnetic field. Their formal name, magnetorheological fluids, is a mouthful, but most ferrofluids are made of iron or iron oxide particles suspended in a thick fluid or encased in a surfactant. Ferrofluids flow like any other liquid until there is a magnet in the vicinity. Bring in a magnet and the ferromagnetic materials undergo a phase change. They rearrange in three-dimensional space. The particles line up, forming spikes that can project well above the surface of the material. NASA has promoted ferrofluid as a potential future “robot blood,” and a variety of luxury car dealers are making use of the unique properties of this material in smart shock absorbers. But in the lab, it is just fun to play with.

Other fun smart materials (not necessarily nanoscale) are called non-Newtonian fluids. Newtonian fluids are fluids where the viscosity is constant. Water is a Newtonian fluid. You can lower your finger into a pot of water slowly or quickly. Whether you move slowly or quickly, the molecules of water can move out of the way and let your finger into the fluid. Non-Newtonian fluids exhibit significant changes in viscosity in response to an applied shear rate. In other words, they resist your attempt to put your finger in the fluid, and the faster your finger tries to move, the more non-Newtonian fluids resist. Common examples, samples you can make in your kitchen, include starch-based custards and Oobleck, made of cornstarch and water. Oobleck is a fluid that you can pour or put your hand into as long as you move slowly—but the material behaves like a solid when a large impulse is applied. For instance, it is impossible to penetrate the surface by trying to karate-chop the material.

I once had a student make a washtub full of Oobleck and prop it up against a tree on his parents’ farm. He made a video showing his ability to submerge his hand into it, as long as he moved his hand slowly. But when he tried to hit the Oobleck, his hand bounced off the surface. To convince us that he wasn’t acting, in the next scene he took a video showing the bullets from a 20-gauge shotgun bouncing off the surface of the material.

How does Oobleck behave this way? What does “significant changes in viscosity in response to an applied shear rate” mean? Imagine the molecules of Oobleck as long, thin, sticky strands like wet spaghetti noodles. If you slowly try to put your finger into a pot of sticky spaghetti noodles, you can do it. The noodles can rearrange and move out of the way of your finger. But if you try to punch your fist into the spaghetti, it is harder to penetrate into

the material. The noodles are tangled around each other, and it is hard for them to move out of each other's way and let your fist in.

As you might imagine, there is also a serious side of Oobleck. The military is very interested in developing non-Newtonian fluids that can be woven into protective gear, or coated onto vehicles to protect them. Non-Newtonian fluids could have a substantial advantage over the super-tough materials used in today's protective gear. When not being stressed by an impact, these materials remain fluid and soft. It is certainly conceivable that tomorrow's military and police uniforms containing non-Newtonian armor could wear like a polo shirt or jeans. But if you were shot at while wearing it, this same material would protect you completely from the bullets.

In an alternate approach, engineers from the University of Sydney, Australia, are hoping to exploit the elasticity of carbon nanotubes to substantially improve anti-ballistic materials. Today's materials act by spreading the bullet's force horizontally across the material. Blunt force trauma—perhaps severe bruising or, worse, damage to critical organs, is still a frequent consequence of impacts.

New smart materials will utilize the elasticity of the molecular components to mitigate even the blunt force trauma. The atoms that make up carbon nanotubes are held together by covalent molecular forces. These very strong forces make individual carbon nanotubes quite mechanically robust, stronger structurally than steel. But the real benefit of carbon nanotubes is that they have sticky surfaces. They bind together into strong “ropes” because of the van der Waals force they share. Van der Waals is the weak attraction that molecules have for one another when they are brought close together, used, for example, by geckos when they stick to a ceiling. The van der Waals forces are responsible for the stickiness of the nanotubes. Because of the relatively large surface area of the nanotube, and the strength of the van der Waals forces, carbon nanotubes are exceptional in their elasticity. Not only do they resist deformation, they push back, providing a force that prevents more than a molecular-scale penetration of the nanofibers.

Self-healing materials extend a product's life by repairing damage from normal use. Most self-healing materials depend inherently on the art of self-assembly, when fundamental intermolecular forces cause nanomaterials to rearrange themselves to a low-energy configuration. A self-healing tire will seal around a nail head and prevent the tire from going flat. This is usually accomplished by having a layer of highly viscous material sandwiched between rubber layers in the tire. When the tire is stabbed by a nail, the viscous material flows against the metal and makes a strong seal. The seal is sufficient to prevent the air in the tire from escaping.

Consumer packaging is another arena in which smart materials are finding application today. You can purchase plastic containers with lids impregnated with nanoscale zeolites. Zeolites are naturally occurring inorganic ceramic

materials with rigid structures that form a pattern of cavities within the solid structure. Specific zeolites preferentially absorb or decompose ethylene gas. When present in packaging or shipping materials, they thereby reduce the rate at which fresh fruits spoil.

Another form of smart packaging is designed to protect products from damage by ultraviolet light (UV). Just as you can damage your skin by excessive exposure to UV light from the sun, many products are also adversely affected by exposure to UV light. Patents have been issued describing processes whereby nanoparticle-sized titanium dioxide, TiO_2 (nano- TiO_2), is embedded in a plastic material to provide a clear, strong, flexible plastic packaging material that absorbs UV radiation.

Titanium dioxide is a well-known white pigment and is the active ingredient in white paint. As a bulk material it is very efficient at absorbing visible light. Nano-sized TiO_2 particles that are 1 to 100 nm in dimension can be dispersed in water while remaining transparent in appearance. Nano- TiO_2 is not very good at absorbing visible light, but it is very effective at both absorbing and scattering shorter wavelength ultraviolet radiation. Therefore, embedding nano- TiO_2 in plastics can improve the quality of packaging materials. It provides a transparent UV barrier film. The smart part of using nano-scale TiO_2 is that by decreasing the particle size, there is an increase in the surface-area-to-volume ratio, so the amount of filler needed can be small. A small amount of filler mitigates its interference with the properties of the plastic material that is the majority component in the packaging. Nano quantities of filler have negligible effect on the weight or thickness of packaging materials, improving properties without adding measureable weight or volume to the product.

It is probably not an exaggeration to say that most of the science of nanotechnology can be categorized as a search for smart materials. As we learn more about the unusual properties of nanomaterials and composites made from them we will continue to find innovative, smart ways to solve problems using the new technologies.

FOR GREATER UNDERSTANDING

Questions

1. What is a “smart” material?
2. Why are piezoelectric materials used for “smart” materials?
3. What is nitinol?
4. How does a nanomaterial’s surface-area-to-volume ratio contribute to its success as an absorbent?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

Haghi, A.K., and Gennady E. Zaikov. *Nano-scaled and Smart Materials*. New York: Novinka Books, 2010.

Articles of Interest

Buehler, William J., and Frederick E. Wang. “A Summary of Recent Research on the Nitinol Alloys and Their Potential Application in Ocean Engineering.” *Ocean Engineering*. Vol. 1, iss. 1, pp. 105–108, July 1968.

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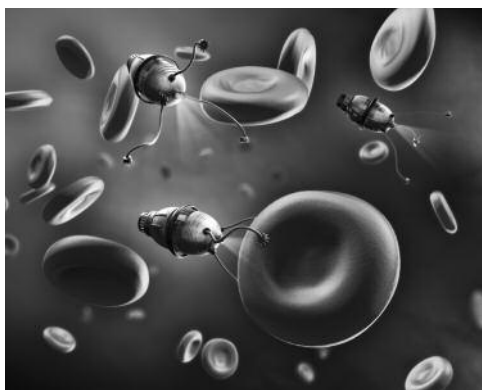
1. Nitinol Devices & Components, Inc. (NDC) in Fremont, California, provides a reference library through their “Nitinol University” tab. There is a comprehensive listing of papers dedicated to nitinol research. — <http://www.nitinol.com/nitinol-university/university-resources>
2. A *YouTube* video by Sachiko Kodama and Yasushi Miyajima entitled “Morpho Towers—Two Standing Spirals” shows how ferrofluids can be manipulated. — <http://www.youtube.com/watch?v=me5Zzm2TXh4>
3. The *Photonics.com* website provides an article from 2003 entitled “MIT Explores Ferrofluid Applications.” — <http://www.photonics.com/Article.aspx?AID=15447>
4. The *Fast Company* magazine website provides an article by Kit Eaton from July 2010 entitled “U.K. Scientists Demo Bulletproof Liquid Armor.” — <http://www.fastcompany.com/1668668/bullet-proof-liquid-armor-kevlar-bae-non-newtonian>

Lecture 14

Nanotechnology Ethics

The Suggested Reading for this lecture is Mark Ratner and Daniel Ratner's *Nanotechnology: A Gentle Introduction to the Next Big Idea*, chapter 11: "Nanotechnology and You."

In the twenty-first century, scientists and engineers are engaged in efforts to bring nanotechnology to fruition to improve the human condition. Imagine a world in which cars can be assembled molecule-by-molecule, garbage can be disassembled and turned into beef steaks, and people can be operated on and healed by cell-sized robots. Sound like science fiction? Well, with current semi-



conductor chip manufacturing encroaching upon the nanometer scale and the ability to move individual atoms as first demonstrated by IBM scientists, the time is fast approaching when technological ability to fabricate productive machines and devices that can manipulate things at the atomic level will be here. Atomic control will allow development of molecular-sized computers and robots. Molecular-sized robots will give us unprecedented control over matter and the ability to shape the physical world to the very limits imposed by nature. Some may see this as pure fantasy, but my sense is that we are experiencing the next technological revolution.

Are there hazards associated with these undertakings? Yes. Biological systems are, after all, structured by Mother Nature to operate at the nano-level. The impact of manufactured nanodevices not found in nature is truly unpredictable at this time. However, the historical foreshadowing of the development of nanotechnology by scientists like Richard Feynman places the field in a unique position to develop in association with the ethical decision-making processes, and with an informed awareness of any hazards and the opportunity to mitigate them before they become health, environmental, or social disasters.

In 1986, K. Eric Drexler, a researcher at MIT, anticipated the development of molecular machines and published *Engines of Creation*, in which he outlined the possibilities and consequences of this emerging field. Drexler is sometimes credited with coining the term "nanotechnology." Drexler's interest was inspired by Nobel laureate Richard Feynman's 1959

lecture, “There’s Plenty of Room at the Bottom.” Since then, Drexler has written numerous books on the subject of nanotechnology and has founded the Foresight Institute, a nonprofit organization dedicated to the responsible development of nanotechnology. It hosts conferences and competitions to raise the awareness of nanotechnology and the ethical issues involved in its development.

The Nanoethics Group is a non-partisan organization based at California Polytechnic State University in San Luis Obispo. The Nanoethics Group studies the ethical and societal implications of nanotechnology. They have also published a series of books on ethics and nanotechnology and sponsor events designed to engage the public as well as nanotech corporate decision makers and researchers in discussions on the implications of nanotech developments.

Beginning in 2001, the U.S. government began to explicitly promote interest in nanotechnology when it created the National Nanotechnology Initiative (NNI). The government has taken an active role since then in promoting, sponsoring, monitoring, and guiding research and development in this field. A number of federal funding agencies support nanoresearch, including the National Science Foundation (NSF), the Department of Energy (DoE), the Department of Defense (DoD), NASA, the National Institutes for Occupational Safety and Health (NIOSH), the National Institute of Standards and Technology (NIST), and the National Institutes of Health (NIH). There are eleven research universities that make up the National Nanotechnology Initiative Network. This infrastructure has an enormous influence on the direction of scientific research done in the United States. With so many resources dedicated to its development, nanotechnology will have an impact within this century, so it is important to examine its ethical implications as it evolves.

What are some of the ethical issues related to nanotechnology? Among the primary concerns are the influence of nanocomputers on personal privacy issues, the safety of nanomachines, and the unintended environmental and health impacts caused by nanomaterials in our everyday environment.

The potential benefits of nanotechnology are obviously substantial or it would not be attracting our attention. Perhaps the most impressive benefit is the application of nanotechnology to accomplish “green chemistry” goals. Green chemistry focuses on the concept of “atom economy.” In other words, it seeks to develop strategies for chemical synthesis that are 100 percent atom efficient. All the atoms from the raw materials at the start of a process are converted 100 percent into product molecules. There is no excess material at the beginning or left over at the end. Why is atom economy a green chemistry concept? By and large the material we consider to be pollutants, the chemicals discharged through smokestacks or into waste streams, are byproducts of chemical manufacturing processes. Most of chemistry is not 100 percent efficient. It is quite a bit like cooking. If you

want to make an apple pie, you can save any extra flour and shortening from the pie crust for future baking. But the apple peels and cores represent a waste stream from your pie-baking process. You may just dump them in the trash or run them down the disposal. If you are a gardener, you may put them in a compost heap. But if you are a chemistry lab, you need to be mindful of the cyanide content of apple seeds or pips. They typically contain 700 mg of cyanide per kilogram. The more efficient you are at separating the apple fruit from its core, the higher the relative concentration of cyanide in your waste. The higher the concentration of cyanide in your waste, the more attention you need to pay to the way in which you dispose of it. The difference between being 95 percent efficient and 100 percent efficient is actually much larger than the difference between being 90 percent efficient and 95 percent efficient. No waste is an entirely different manufacturing environment than less waste.

In a lab, if you want to synthesize acetyl salicylic acid, aspirin, for instance, a classical approach begins with salicylic acid and acetic anhydride. The anhydride is present in excess, which means some is left over at the end of the reaction (like the flour in your apple pie). Under typical lab conditions you find that about 70 percent of your starting material is converted into aspirin. The rest of the material gets converted to other products that you aren't interested in. Therefore it is waste. Today, we often deal with the waste produced by chemical processes by understanding that one process's waste may be another process's raw material. And we charge substantial fees to labs and plants disposing of waste materials to motivate them to find creative alternate uses for them.

Nanotechnology offers the promise of building machines that could manipulate materials on a molecule-by-molecule or atom-by-atom basis and provide 100 percent conversion from raw materials to products with no waste chemicals generated. These same nanomachines could be built to mimic certain cellular components in biological systems—they could recognize toxins in the environment and disassemble them into benign smaller pieces, or even take them apart to individual atoms. Breaking things you don't want into small components you could reuse in myriad other ways is the ultimate in recycling.

Other obvious beneficial applications of nanotechnology are in the fields of medicine and health. In the same way that nanomachines could perform chemical synthesis, they could perform atom-by-atom pharmaceutical synthesis. Pharmaceutical and medically related manufacturing represents up to 30 percent of the total chemical enterprise today. But in addition to improving the manufacture of pharmaceuticals, nanotechnology promises a variety of improvements in medical treatment strategies. We have already discussed the use of nanodevices in the early detection of cancer and in its treatment. The benefit is in scientists' ability to customize nanoscale devices. They are manufactured so they only recognize and attach to specific cancerous cells.

And they travel with a payload designed to cause devastating but highly localized damage to the cancer cells when activated. The diagnostic advantage is substantial. The nanoparticles act like super-magnifying glasses, allowing oncologists to see the extent of the problem to a resolution not previously possible. And the selectivity minimizes the side effects by targeting treatment only to those cells that pose a danger, not to all the cells in the body. The problem of side effects from chemotherapy and radiation will be mitigated as nanotechnology-based cancer treatments are developed and perfected. The conceptual work is easy; the actual research and development to demonstrate safety and efficacy in humans will take time. As envisioned by Drexler, as well as many others, we can expect to see biologists develop nanocomputers no bigger than bacteria and nanomachines (sometimes called “nanites” after terminology coined in the television show *Star Trek: The Next Generation*) that could be used as molecular assemblers and disassemblers to build, repair, or tear down any physical or biological objects.

In essence, the purpose of developing nanotechnology is to have tools to work on the molecular level analogous to the tools we have at the macro-world level. Like the robots used to build cars and the construction equipment used to build skyscrapers, nanomachines will enable us to create a plethora of goods and expand our engineering abilities to the smaller limits of the physical world.

The environmental upside of nanotechnology is pretty obvious. Nanobots that could disassemble everything in our waste stream down to simple components on a reasonable time scale could provide a limitless source of useful recycled materials. Today’s discarded car could become tomorrow’s pen, which could become next year’s bread. Waste would cease to exist—it would just become a resource for future applications. Nanobots could be deployed to disassemble truly toxic chemicals and convert them to useful raw materials. They could then be used to assemble new products that are needed with 100 percent efficiency. The only toxin arena where it is difficult to imagine nanotechnology having a substantial impact is in nuclear waste. The products of nuclear processes include high-energy photons and particles that would be energetic enough to destroy any nanodevice with which they came in contact. The nanodevices would resemble structures destroyed by meteors on the nanoscale.

With all this promise, what are the ethical concerns about nanotechnology? Depending on your politics and perspectives, you can imagine a variety of hazards. The advantage of nanomachines disassembling and assembling what we want them to is matched by the possibility that they will run amok and disassemble or assemble things we do not want them to. The technology that creates spectacular applications in medicine could also be used to create spectacular weapons, or be used as weapons themselves. Those with privacy concerns over the current use of communications technology and social media will have even more to consider if nanoscale computing makes it

possible to embed logic circuits in nearly everything and allow undetectable electronic surveillance to become an affordable component of our society.

But enough of this hypothesizing. Let's consider a specific, real application of the ethics of nanotechnology.

In the early 2000s, nanosilver became a hot item in the nanotechnology universe. The old expression "born with a silver spoon in his mouth" does not refer to the wealth that allows ownership of this valuable metal—it refers to the health effects conveyed by using silver spoons and silverware in serving food. Silver's antibacterial and antiviral properties have been known at least since the time of Hippocrates.

Colloidal solutions of silver have had some popularity in the alternative health field after being banned by the FDA in 1999. Colloidal silver is tasteless and mild. A few years ago, the so-called blue man, Paul Karason, from California, made a splash on daytime TV. Apparently his habit of consuming colloidal silver to treat dermatitis has had the interesting side-effect of turning his skin blue. Although silver is considered a heavy metal and exposure can contribute to liver and kidney failure, Karason claims he feels fine.

Given silver's history as an antibacterial, antiviral, and antifungal agent, it was inevitable that a method of producing stable nanosilver would permit applications of it in a wide variety of consumer products. Because nanosilver is so small, a very large surface area can be covered with enough silver to make it bioactive at reasonable cost, at least before the increase in precious metal prices in the early 2010s. In the early 2000s, nanoscale silver was either embedded in or coated on a variety of consumer products, including Band-Aids, socks, and washing machines because of its antibacterial properties. You can imagine using it as a coating on or a component of all sorts of surfaces and devices in hospitals to help reduce the incidence of secondary infections. However, the nanosilver craze seems to have run its course. In 2011, these products are more difficult to find.

Why is this? There are undoubtedly several reasons. One is the increasing cost of silver, but the other is concern about the environmental impact of nanosilver.

Silver nitrate, the most common salt of silver, is soluble in water, producing silver ions that are known to be toxic to fish as well as to bacteria and viruses. In 2006, data reporting the results of exposing fish to nanosilver samples showed that nanosilver was also toxic, and even lethal, to fish. The negative impact happened when fish were exposed at several stages of their development. It was observed that nanosilver particles were able to cross the egg membranes and move into the fish embryos after less than a day's exposure. LC50 values (a concentration of a material that will kill 50 percent of the test subjects) ranged from 1.25 mg/L to 10.6 mg/L depending on the specific type of nanoparticles used. This study demonstrated that

nanosilver, perceived as a beneficial compound when the focus is on antibacterial use, is also a potential environmental and biological hazard.

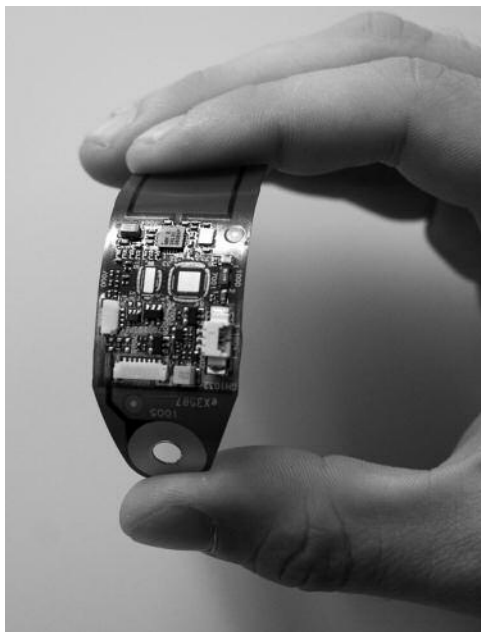
In August 2010, the EPA released a draft of its “Nanomaterial Case Study: Nanoscale Silver in Disinfectant Spray,” a comprehensive environmental assessment on the use of nanosilver as a disinfectant spray. Comprehensive environmental assessments (CEA) combine a product life-cycle perspective with risk assessment. The EPA study is intended to clarify what is scientifically known about nano-Ag and what remains to be determined. The study focuses on the specific application of nano-Ag in disinfectant sprays. After public comments are collected, the EPA may issue rulings.

What about nanocomputing? Smaller, faster computational power is surely benign, isn't it? And nanoscale cameras and recording devices would simply reduce the costs of recording images, right? The intent of red-light cameras is to make intersections safer by taking a picture of any car that goes through the intersection on a red light, and using registration records, mail a traffic ticket to the owner. There are cities with a large number of surveillance cameras to provide a deterrent to criminal activity. In December 1996, British writer David Brin posed an interesting question relevant to the future of nanodevices in society in an essay called “The Transparent Society.” In the essay, he discusses two possible futures for a society in which cameras are watching public spaces 24/7. In one scenario, crime is cut substantially as images are beamed continuously to central police stations throughout the community. The authorities are certain to observe, record, and pursue any wrongdoers. In the other scenario, the video feeds are available through hand-held devices to any citizen who chooses to look at the live image being transmitted by a camera. A woman walking home in the evening can look around the corner and verify that her route is free of threatening characters. A shoplifter can never know whether another citizen is watching—or not. Similar reductions in crime are reported in this community. But Brin asks us to consider which community we would rather inhabit.

Eric Drexler is a leading proponent of the ethical use of nanotechnology. In his writings, he identifies weapons as a negative use of nanotechnology. Improving today's weapon capabilities by miniaturizing guns, explosives, and the electronic components of missiles will be deadly enough. However, it is possible to envision nanoscale disassemblers that could attack physical structures or even biological organisms at the molecular level. Disassemblers run amok is a vision of the future known as “The Gray Goo Scenario.” Drexler describes futurists who imagine nanomachines designed to be self-replicating, multiplying endlessly like viruses. Even without considering these extreme disaster scenarios, as with any new technology, we can find plenty of potentially harmful uses for it. It could be used to erode our freedom and privacy; people could use molecular-sized microphones, cameras, and homing beacons to monitor and track others.

Or, if we are proactive and go through the exercise of formulating solutions to potential ethical issues before nanotechnology is mindlessly adopted by society, we could create policies that will optimize the implementation of these new technologies, while minimizing its negative effects. The Foresight Institute identifies catastrophic accidents and misuse as the two greatest threats from development of nanotechnology. It advocates the formation of a nongovernment advisory council to monitor the research and help formulate ethical guidelines and policies. It states that “nanomachines should *not* be designed to be general purpose, self-replicating, or to be able to use an abundant natural compound as fuel.” It proposes that nanomachines be tagged with a radioactive isotope sample so they can easily be tracked in the environment.

Nanotechnology promises spectacular benefits. However, nanotechnology can be developed using guidelines to ensure that its implementation is not accompanied by unanticipated negative side effects. As with any new technology, it will be impossible to stop ill-intentioned organizations who may seek to divert the technology for harmful purposes. However, if the researchers in this field put together an ethical set of guidelines (for example, Molecular Nanotechnology Guidelines) and follow them, then we should be able to develop nanotechnology safely while still reaping its benefits.



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A Belgian nanotechnology research center has developed a wireless electrocardiogram (ECG) patch—a miniature device that can be worn like a watch. It monitors heart patients twenty-four hours a day and sends the data to a computer for analysis. The ECG patch gives the person freedom to engage in daily activities and poses no limitation to mobility.

FOR GREATER UNDERSTANDING

Questions

1. Why might some consider nanotechnology a hazardous technology?
2. Would you sell colloidal silver as a “health tonic”? Why or why not?
3. Would you prefer to live in a society where the police had 24/7 video access to all public activities, or one in which individuals had access to the same information? Or do you think such things should be prohibited? What are the benefits and costs of your position?

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

Bennett-Woods, Deb. *Nanotechnology: Ethics and Society*. Perspectives in Nanotechnology. Boca Raton, FL: CRC Press, 2008.

Websites of Interest

1. The *Foresight Institute* website provides a copy of its “Molecular Nanotechnology Guidelines” in pdf format. — <http://www.foresight.org/guidelines>
2. The *Nanoethics Group* website based at the California Polytechnic Institute features book reviews, stories, and other information on the ethics of nanotechnology. — <http://www.nanoethics.org>
3. *Wired* magazine provides an article by David Brin from December 1996 entitled “The Transparent Society,” which continues to be relevant to privacy issues today. — <http://www.wired.com/wired/archive/4.12/fftransparent.html>

GLOSSARY

Assembler: A general-purpose device for molecular manufacturing, capable of guiding chemical reactions by positioning molecules.

Atom: The smallest unit of a chemical element, about a third of a nanometer in diameter. Atoms make up molecules and solid objects.

Atomic Force Microscopy/Microscope (AFM): Atomic force microscopy is a technique for analyzing the surface of a rigid material down to the level of the atom.

Biomimetics: The design of systems, materials, and their functionality to mimic nature.

Bottom Up: Building organic and inorganic structures atom-by-atom, or molecule-by-molecule.

Carbon Black: A powdered form of elemental carbon. The primary use of carbon black is in rubber products, mainly tires and other automotive products, but also in many other rubber products such as hoses, gaskets, and coated fabrics. Much smaller amounts of carbon black are used in inks and paints, plastics, and in the manufacture of dry-cell batteries.

Colloid: A mixture in which one substance is divided into minute particles (called colloidal particles) and dispersed throughout a second substance.

Composites: Combinations of metals, ceramics, polymers, and biological materials that allow multi-functional behavior.

Diode: A diode is a specialized electronic component with two electrodes called the anode and the cathode. Most diodes are made with semiconductor materials such as silicon, germanium, or selenium.

DNA: Deoxyribonucleic Acid. DNA is a code used within cells to form proteins.

Dry Nanotechnology: Derives from surface science and physical chemistry, focuses on fabrication of structures in carbon silicon and other inorganic materials.

ESM: Electro Scanning Microscope.

Fullerene: A Fullerene is a pure carbon molecule composed of at least 60 atoms of carbon. They are cage-like structures of carbon atoms; the most abundant form produced is Buckminsterfullerene (C₆₀), with sixty carbon atoms arranged in a spherical structure. Because a Fullerene takes a shape similar to a soccer ball or a geodesic dome, it is sometimes referred to as a buckyball after the inventor of the geodesic dome, Buckminster Fuller.

Ion: An atom or group of atoms in which the number of electrons is different from the number of protons. If the number of electrons is less than the number of protons, the particle is a positive ion, also called a cation. If the number of electrons is greater than the number of protons, the particle is a negative ion, also called an anion.

LED (Light Emitting Diode): A semiconductor device that emits visible light when an electric current passes through it.

Lithium Ion (Li-Ion) Battery: A rechargeable battery with twice the energy capacity of a Nickel-Cadmium battery and greater stability and safety.

MEMS: Micro Electro Mechanical Systems—Technology used to integrate various electro-mechanical functions onto integrated circuits.

Mesoporous: Mesoporous materials are porous materials with regularly arranged, uniform mesopores (2 to 50 nm in diameter). Their large surface areas make them useful as adsorbents or catalysts.

Molecule: A group of atoms held together by chemical bonds, a molecule is the typical unit manipulated by nanotechnology.

Moore's Law: The observation made in 1965 by Gordon Moore, cofounder of Intel, that the number of transistors per square inch on integrated circuits had doubled every 18 months

since the integrated circuit was invented. Moore predicted that this trend would continue for the foreseeable future.

Nano: A prefix meaning one billionth ($1/1,000,000,000$).

Nanobiotechnology: Applies the tools and processes of nano/microfabrication to build devices for studying biosystems.

Nanocomputer: A computer made from components (mechanical, electronic, or otherwise) built at the nanometer scale.

NanoElectroMechanical Systems (NEMS): A generic term to describe nanoscale electrical/mechanical devices.

Nanofibers: Hollow and solid carbon fibers with lengths on the order of a few microns and widths varying from tens of nanometers to around 200 nm.

Nanofluidics: Controlling nanoscale amounts of fluids.

Nanolithography: Nanolithography is the art and science of etching, writing, or printing at the microscopic level, where the dimensions of characters are on the order of nanometers.

Nanopores: Nanoscopic pores found in purpose-built filters, sensors, or diffraction gratings.

Nanotechnology: Areas of technology where dimensions and tolerances in the range of 0.1 nm to 100 nm play a critical role.

Nanotube: A one-dimensional fullerene (a convex cage of atoms with only hexagonal and/or pentagonal faces) with a cylindrical shape.

Organic LED: LED made from carbon-based molecules, not semiconductors.

Photonics: Electronics using light (photons) instead of electrons to manage data.

Piezoelectricity: The generation of electricity or of electric polarity in dielectric crystals subjected to mechanical stress, or the generation of stress in such crystals subjected to an applied voltage.

Quantum Dot: A nanoscale crystalline structure that can transform the color of light.

Scanning Tunneling Microscope (STM): A device that obtains images of the atoms on the surfaces of materials—important for understanding the topographical and electrical properties of materials and the behavior of microelectronic devices.

Semiconductor: A substance, usually a solid chemical element or compound, that can conduct electricity under some conditions but not others.

Self-assembly: Refers to the use in materials processing or fabrication of the tendency of some materials to organize themselves into ordered arrays (for example, colloidal suspensions).

Smart Materials: Reactive materials that combine sensors and actuators, and possibly computers, to enable a response to environmental conditions and changes to those conditions.

Substrate: In nanotechnology the base material where applications are built up.

Top Down: Refers to making nanoscale structures by machining and etching techniques.

Wet Nanotechnology: The study of biological systems that exist primarily in a water environment.

Zeolite: Any one of a family of hydrous aluminum silicate minerals, whose molecules enclose cations of sodium, potassium, calcium, strontium, or barium, or a corresponding synthetic compound, used chiefly as molecular filters and ion-exchange agents.

Source: Selected glossary terms courtesy of the Institute of Nanotechnology, University of Stirling, Stirling, Scotland, UK — <http://www.nano.org.uk/nano/glossary>.

COURSE MATERIALS

Suggested Reading

Ratner, Mark, and Daniel Ratner. *Nanotechnology: A Gentle Introduction to the Next Big Idea*. Upper Saddle River, NJ: Prentice Hall, 2003.

Other Books of Interest

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