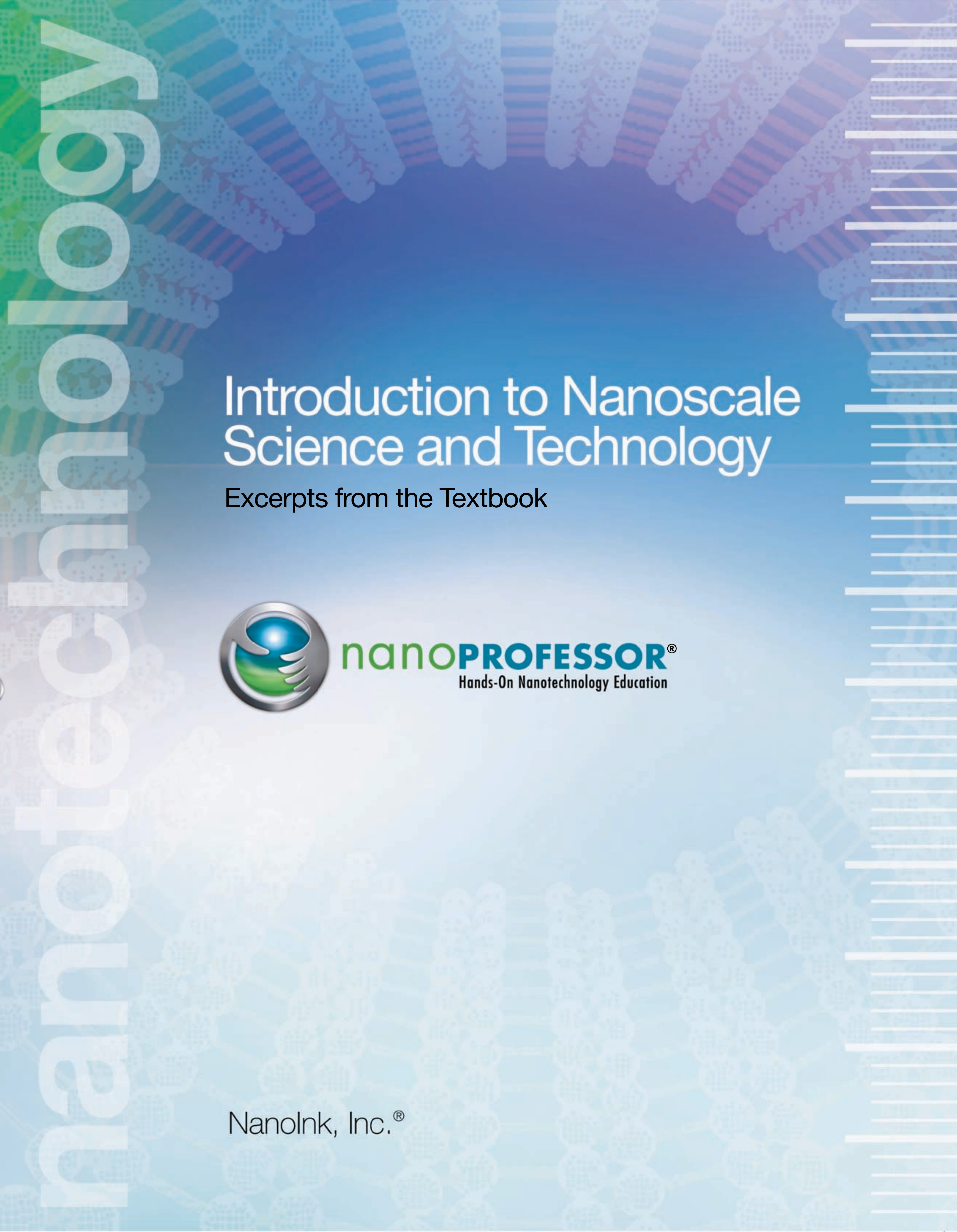


Introduction to Nanoscale Science and Technology

Excerpts from the Textbook

nanoPROFESSOR®
Hands-On Nanotechnology Education

NanoInk, Inc.®

Contents

Chapter 1

The Nanoscale

You are about to explore nature in a realm you cannot directly perceive. This realm of nature is called the nanoscale, and it encompasses things that are so small that their length is measured in units of one billionth of a meter. What could be that small? Actually, about everything you can see, as well as most of the things you can't see, are made up of component parts—molecules and groups of atoms—that fall within the range of the nanoscale. Think about this for a moment. By extending your perceptions to the nanoscale, you are increasing your understanding of how atoms and molecules serve as the very building blocks of matter.

Even more interesting, you will soon discover that nature at the nanoscale can behave quite differently than what you might expect. In this course, you will not only explore some of the phenomena that occur at the nanoscale, you will also learn how to actually manipulate and affect materials at the nanoscale. Why would you want to do that? The answer is very exciting: to create the ingenious and groundbreaking materials and products of the future! First, there is much to do to prepare for this amazing and challenging opportunity.

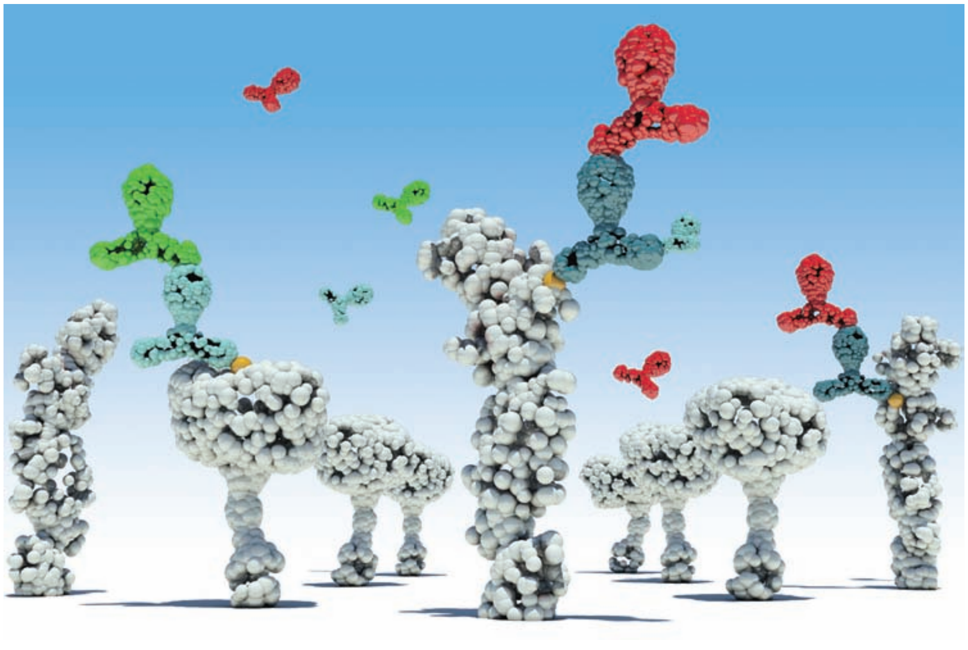


Figure 1.1 An array of nanomaterials on a surface can be used as a biosensor. Working at the nanoscale presents extraordinary possibilities for the creation of new materials and products.

Section 1

Exploring the Nanoscale

TAKE-HOME MESSAGES

1. The nanoscale is very, very small.
2. Just the size and scale of matter can dramatically change how it behaves.
3. Nanotechnology means work performed at the nanoscale to make useful applications.

POINTS TO PONDER

- What is the nanoscale? What dimensions does it include?
- What does nano mean in words like nanometer, nanoscale, nanoscience, and nanotechnology?
- What are some objects that are small enough to be measured in the nanoscale?
- How is nanotechnology defined?
- What scientific disciplines are used in nanoscience?

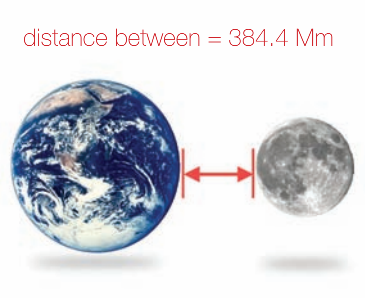
The nanoscale lies between the microscopic scale and the atomic scale. In a sense, this realm was passed over in a rush to understand the smallest known particles: individual atoms, subatomic particles (protons, neutrons, and electrons), and the building blocks of protons and neutrons (quarks). While these subatomic and atomic scales are indeed fascinating, we are going to focus on the nanoscale and why it is a unique domain.

What Is the Nanoscale?

The definition of nanoscale lies in the prefix nano, which comes from the Greek word for dwarf and is used in the metric system to mean one billionth. Just as milli means one thousandth and centi means one hundredth, nano is used to

Examples of Scale (referenced in Figure 1.2)

1 megameter



2 meter

3 centimeter

Prefix	Symbol	Exponential Factor	Length Examples	Length Scale
yotta	Y	10^{24}	137 yottameters (Ym) is the estimated size of the universe.	Generally referred to as the **astronomical** scale,distances at this scale are so vast their size cannot be observed directly and can be determined only through mathematical extrapolation.
zetta	Z	10^{21}	1 zettameter (Zm) is approximately 100,000 light years, or the diameter of the Milky Way galaxy.	
exa	E	10^{18}	1 exameter (Em) is approximately 100 light years.	
peta	P	10^{15}	Light travels 9.5 petameters (Pm) in one year. By some estimates it is the distance from the Sun to the Oort Cloud – the outermost region of our solar system.	
tera	T	10^{12}	1.08 terameters (Tm) is approximately the distance light can travel in 1 hour, or one light hour.	
giga	G	10^{9}		
mega	M	10^{6}	The distance between Earth and moon is 384.4 megameters (Mm). **1**	
kilo	k	10^{3}	The kilometer is the unit most commonly used throughout the world to measure driving distances.	Generally referred to as the **macro** scale, this scale is visible to the unaided eye.
hecto	g	10^{2}		
deca	da	10^{1}		
		$10^{0} = 1$	The length of an average bicycle is 1.6 meters (m). **2**	
deci	d	10^{-1}		
centi	c	10^{-2}	Earbuds have a diameter of approximately 1.8 centimeters (cm). **3**	
milli	m	10^{-3}	A penny is approximately 1.8 millimeters (mm) thick. **4**	
micro	µ	10^{-6}	Red blood cells have a diameter of 6 – 8 micrometers (µm). **5**	Generally referred to as the **micro** scale, this scale becomes visible with the use of optical microscopes.
nano	n	10^{-9}	The width of a strand of DNA is 1– 2 nm. **6**	The **nanoscale** ranges from 1–100 nanometers (nm).
	Å	10^{-10}	The angstrom (Å) is a non-SI unit. 1 angstrom equals 0.1 nanometer (nm).	The **atomic** scale is often measured in angstroms.
pico	p	10^{-12}	The distance from proton to electron in a hydrogen atom is approximately 50 picometers (pm)	
femto	f	10^{-15}	The diameter of the nucleus is in the range of 1.6 femtometers (fm) as in hydrogen to about 15 femtometers (fm) as in uranium.	The **subatomic** scale
atto	a	10^{-18}		
zepto	z	10^{-21}		
yocto	y	10^{-24}		

Figure 1.2 This table shows the relationship of metric prefixes to size and to scale. Examples in this table refer only to length. Remember that prefixes can be used with any SI (the International System of Units, or metric system) unit. *See Figure Credits, p. vi.*

4 millimeter

5 micrometer

6 nanometer

alkysilanes, DNA, proteins, and metals are common ink solutions.

Like nanoimprint lithography, soft lithography has issues with pattern transfer. In this case, the presence of residual ink on the surface often affects the print quality. The soft mold is also prone to swelling or other distortions, which can cause patterns to increase in size.

Soft lithography can be either a bottom-up or top-down technique. As a bottom-up technique, a monolayer is deposited on the surface to be patterned. A monolayer is a single layer of molecules. These monolayers can be deposited on various surfaces, such as metallic, glass, or semiconducting surfaces. As a top-down technique, these patterns can be used like a resist to mask and expose regions of the surface for top-down etching and treatment.

Soft lithography is a relatively cheap technique. The molds are inexpensive to create, and they are often discarded after limited use. The variety of inks and compatible surfaces is another benefit. Researchers are attempting to transfer a wider range of molecules to different surfaces using this technique.

Scanning Probe Techniques

Scanning probe microscopes are excellent imaging and measurement devices that have made detailed exploration of the nanoscale possible. Scanning probe microscopes can also be used as nanofabrication tools using both top-down and bottom-up techniques.

Atomic and Molecular Manipulation

Scanning probe microscopes can move atoms and molecules. The tip of an atomic force microscope (AFM) or a scanning tunneling microscope (STM) can be used to rearrange atoms or molecules on a surface. While an AFM can often be brought directly into contact with the surface, an STM usually only interacts with individual atoms and molecules on the surface.

One top-down technique physically etches a surface with an AFM. The tip of these devices can score a resist or a surface leaving a scratch or an impression on them. Extremely hard tips of platinum-iridium or diamond are particularly effective, but the sharpness and hardness of the tip limits this technique. Like a good kitchen knife, a tip becomes blunt over time, which reduces its accuracy and ability to effectively create nanoscale features and patterns. Scratching the surface with a single AFM tip or dragging individual molecules around is a slow process that is useful for research purposes, but it is not a good large-scale manufacturing technique.

Another technique uses a metallic-coated STM tip. When the appropriate voltage is applied to the tip, atoms of the coating material can be transferred to the substrate. Material can also be transferred from the substrate to the tip. In this manner, researchers have deposited and removed nanometer mounds of metals, such as gold, platinum, and silver from a surface.

A further patterning technique that uses an STM selectively removes atoms from a specially prepared surface. A thin layer of hydrogen atoms can be placed on top of a silicon wafer. This is called hydrogen passivation of a surface. By placing a scanning probe tip near the surface of the wafer and applying a voltage, scientists can selectively remove hydrogen atoms. Their removal creates a pattern of dangling bonds on the silicon surface. Various molecules can be introduced into the STM that react with these bonds to form patterns on the silicon surface.

In 1989, Don Eigler, a physicist at IBM, demonstrated the spectacular use of an STM as a bottom-up fabrication tool. He arranged 35 xenon atoms to spell the company name on a surface of nickel. His efforts dramatically showed that atomic manipulation was possible. By slowly positioning individual atoms and molecules, an STM can spell words, draw nanoscale pictograms, and create patterns, which can even confine standing electron waves in atomic corrals.

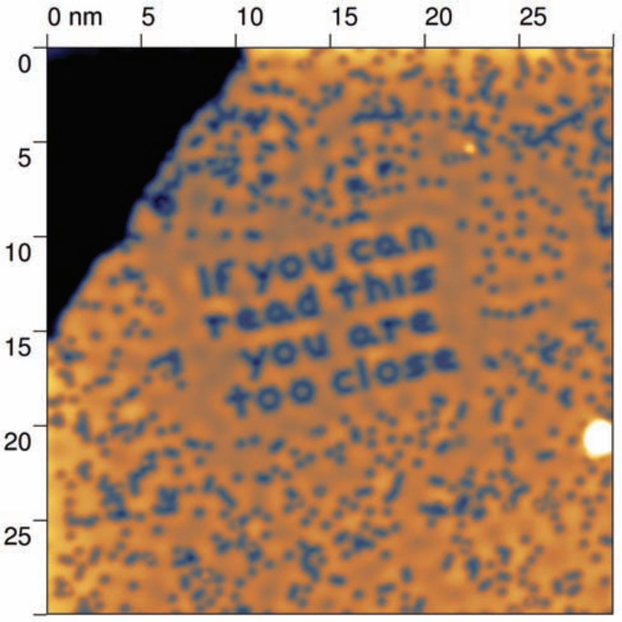


Figure 2.14 An amusing warning at the nanoscale, created by scientists at the IBM Almaden Research Lab, is a rearranged deposit of carbon monoxide molecules on a flat copper surface. Each letter is one nanometer tall and one nanometer wide. *See Figure Credits, p. vi.*

The atomic precision of an STM is also a drawback for large manufacturing. As with e-beam lithography, which uses a single beam, the individual STM tip works serially and takes too long to pattern large areas.

Dip Pen Nanolithography

As the name suggests Dip Pen Nanolithography (DPN), works similarly to a dip or quill pen at the micro and nanoscales. One or more nanoscale pens coated with molecular inks directly writes patterns onto a surface. The nanoscale pen often takes the form of an AFM-like tip that comes to a point about 15 nanometers in radius. MEMS arrays of 8 to 55,000 tips can be used for printing, which allow large parallel

Section 2

A Closer Look at Fluidics

TAKE-HOME MESSAGES

1. The intermolecular forces in fluid or between molecules of fluid and materials (which are often ignored at the macroscale) play a significant role at the nanoscale.
2. Cohesive and adhesive forces are intermolecular attractive forces that result in fluid behaviors such as surface tension, capillary action, and the formation of a meniscus.
3. At the nanoscale, fluids move in a laminar flow and do not mix unless conditions are created to introduce turbulent flow.
4. The Reynolds number is the ratio of inertial forces to viscous forces in fluid.

POINTS TO PONDER

- What properties can we observe in water that are due to its molecular structure?
- How does the structure of the molecules in a fluid impact its properties?
- How does the structure of the channel impact fluid flow?
- What causes a surface to be hydrophobic or hydrophilic?
- What is the relationship between the Reynolds number and laminar or turbulent flow in a system?
- How would you expect gases to behave on the nanoscale, if gases are also fluids?
- How is the Reynolds number affected by temperature?

In the study of fluidics at the macroscale, classical exercises observe water running through a hose and use calculations to determine the volume or force of the water as it leaves the hose. The continuity equation and Bernoulli's equation define classical fluid dynamics. More advanced calculations consider viscosity and temperature as well.

Imagine for a moment, shrinking this scenario (water through a hose) down nine orders of magnitude to the nanoscale. As the channels get more and more narrow, the molecular interactions become much more significant in determining how the fluid moves through the channel. It becomes necessary to consider the intermolecular forces at work, such as cohesion and adhesion. At the nanoscale, calculations focus on the attractive (or repulsive) forces between both the molecules within the fluid and the molecules of the fluid and the channel.

This section discusses some of the phenomena of fluids at the microscale and the nanoscale. The discussion applies our knowledge of atomic and molecular structures (especially water) to the interactions of surface tension, capillary action, and viscosity, as well as laminar and turbulent flow. By studying and understanding the behavior of fluids at the nanoscale, scientists are starting to define the interactions that occur in many biological systems. To understand phenomena at this scale, we must consider and prioritize several kinds of interactions as well as evaluate the physical features of the interacting materials.

Cohesion & Surface Tension

The intermolecular attractive force that unites the molecules of a substance is called cohesion, or cohesive force. For example, water molecules are attracted to each other and join together to form droplets. Water molecules have a relatively strong cohesive force between them, because of the strength of the dipoles they form. It also is this attractive force between the molecules of a liquid that forms surface tension.

Surface tension is a property of liquids and is dependent upon the electrostatic force acting between molecules. Surface tension is a visible result of cohesion (the attraction of molecules to like molecules). The macroscale equation for surface tension is: $\gamma = F/L$ where F is the force required to break the surface tension and L is the length over which that force is acting. However, an exact equation for surface tension that reflects the molecular interactions at the nanoscale does not yet exist.

Consider water in a beaker or flask. The water molecules located in the center of the beaker are interacting with other water molecules which surround them. They are attracting and repulsing each other. By adding the forces on these water molecules from all directions, we find that the net force on a molecule is zero. However, this is not true for the water molecules on the surface

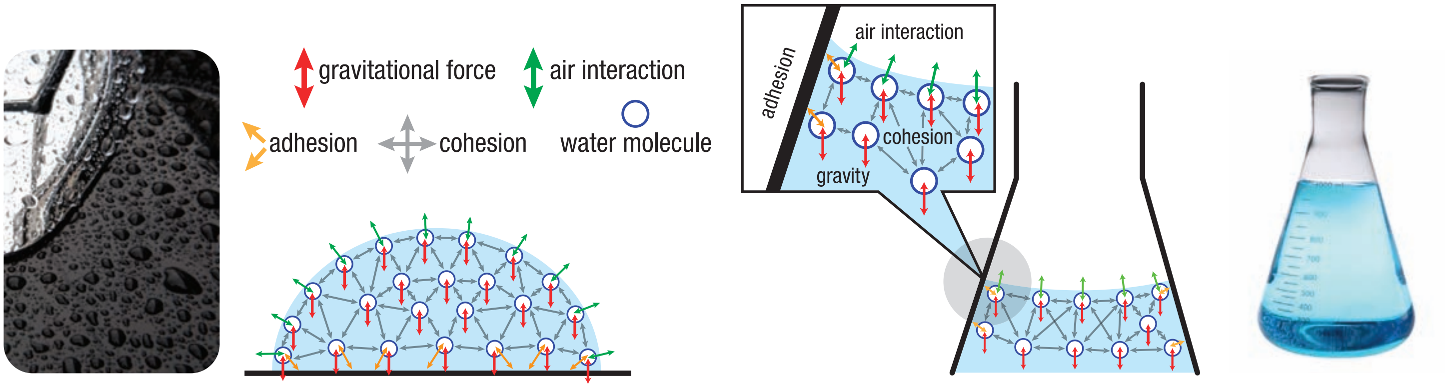


Figure 3.6 The difference in the attractive forces of water molecules with each other and with the air above creates surface tension, as illustrated here. *See Figure Credits, p. vi.*

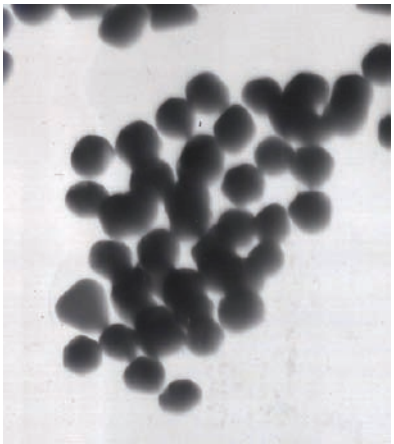


Figure 4.18 An image from a transmission electron microscope (TEM) shows gold nanoparticles that are 80 nanometers in diameter.
See Figure Credits, p. vi.

For many centuries, artisans unknowingly relied on quantum size effects to create red-colored stained glass and luster glazes on pottery. These same effects are now being knowingly used to design and develop biomedical detection systems and electronics that utilize nanoparticles.

Gold nanoparticles are typically prepared by the reduction of Au^{3+} with citrate. The citrate reduces $HAuCl_4$ in water and creates nanoparticles that are approximately 20 nanometers in diameter. Typically, $HAuCl_4$ is dissolved in water by vigorous stirring and heating while slowly adding sodium citrate. The addition of citrate reduces the Au^{3+} ions to neutral gold atoms. As these gold atoms form in solution, they aggregate and precipitate, forming angstrom-sized particles. As more Au^{3+} is reduced to neutral gold atoms, the gold atoms bind to the angstrom-sized gold particles, which cause them to grow in size. As ~20 nanometer-sized gold nanoparticles form, the solution changes color from yellow ($HAuCl_4$) to red-purple.

As the nanoparticles form, citrate ions adsorb on the surface of the gold nanoparticle. The ions provide a surface charge that stabilizes the nanoparticle and stops its further growth. By increasing or decreasing the amount of sodium citrate, the size of the nanoparticle can be controlled, whereby a decreased amount of sodium citrate results in the creation of larger particles.

In order to make nanoparticles in the one- to two-nanometer range, $HAuCl_4$ is reduced in the presence of an alkylthiol, which produces a long chain of repeating Au^{1+}-S-R polymeric intermediates. These intermediates can be reduced to gold-functionalized nanoparticles, or they can be reacted with other metal ions to form bi-metallic nanoparticles such as Au-Pd, Au-Cu, and Au-Ag. If dithiols are used, the addition of a reductant like sodium citrate is unnecessary to form gold nanoparticles that are one to two nanometers in size. By adjusting the ratio of alkylthiol to $HAuCl_4$ to obtain a higher alkylthiol concentration, the size of the resulting nanoparticle can be controlled by inhibiting nucleation, the formation of larger molecular structures.

Nano Fact

Silver nanoparticles exhibit antibacterial properties. They are added to the plastics in food containers, water bottles, countertops, shower curtains, and floor coverings to kill bacteria and limit mold growth. They are also in clothing and building materials, such as caulk, paints, and adhesives.

Nanoparticles formed via the reduction of Au^{3+} by citrate can also be functionalized with alkylthiols by swapping the weakly adsorbed citrate molecules with alkylthiols that have organic functional groups. Functionalization plays two important roles. First, it prevents gold nanoparticles from aggregating as organic stabilizing agents are typically added that bind to the gold nanoparticle surface. The stabilizing agents form a SAM, thereby lowering the free energy of the surface and the reactivity of the nanoparticle. Second, by functionalizing the surface of gold nanoparticles, an organic-inorganic hybrid material is formed. This surface can be used for numerous applications, such as detection devices for biomedical applications, drug-delivery systems, imaging agents, and magnetic data storage.

Quantum Dots

Quantum dots are a special kind of nanoparticle.Quantum dots are frequently prepared from cadmium selenide, cadmium sulfide, lead sulfide, cadmium telluride, or gallium arsenide. Quantum dots have electronic properties that are in-between those of a semiconductor and a molecular crystal. Like metallic nanoparticles, the electronic properties of quantum dots are closely related to their size. However, in a quantum dot a band gap exists between the energy levels of valance and conduction electrons. The larger the quantum dot, the smaller the band gap. The band gap determines how much energy is required to cause electrons to jump from the valence band to the conduction band. This quantum size effect means larger quantum dots require less energy to excite electrons from the valence band to the conduction band. Similarly, when an electron moves from the conduction band down to the valence band, the energy released is equal to the energy band gap. So for the smaller energy band gap found in larger quantum dots, longer wavelengths of light are emitted. Cadmium selenide quantum dots are highly fluorescent in the range 200 to 700 nanometers. The wavelength of their emitted light shifts from red to blue as the size of the quantum dot becomes smaller (Figure 4.19).

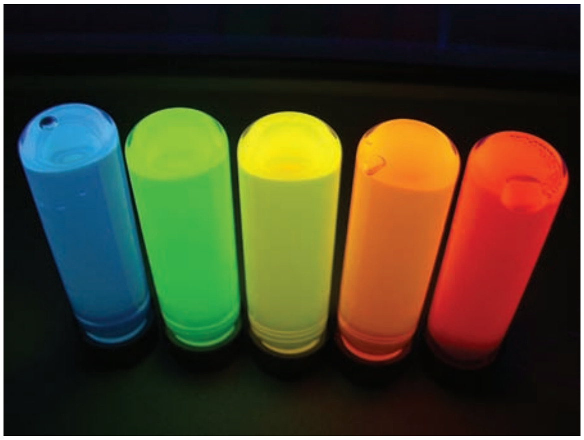


Figure 4.19 The size of quantum dots affects the energy of light they emit. Smaller quantum dots have a blue color; larger quantum dots are red. *See Figure Credits, p. vi.*

Quantum dots are synthesized by suspending the appropriate inorganic precursors such as dimethylcadmium ($Cd(CH_3)_2$) and powdered selenium in

Nano History

Occurring in 1774, Benjamin Franklin is perhaps one of the earliest to document a scientific observation of spreading a monolayer of oil on the air–water interface by demonstrating the effect of a small volume of oil spreading over large distances on a pond. More controlled experiments in following centuries by Agnes Pockels, Lord Rayleigh, and Irving Langmuir enabled scientists to quantify the size of an oil molecule to less than two nanometers.

Pure phospholipids spontaneously assemble in water to form a variety of structures such as those shown in Figure 5.5 (bilayer sheet). Importantly, the polar head group tends to be dissolved in water, while the non-polar alkyl chain will tend to aggregate, leading to a bilayer structure. This bilayer functions as a barrier that surrounds a cell and determines what can and cannot enter or exit the cell. For in vivo environments, about half of the membrane is composed of proteins that are embedded within the membrane and perform various functions such as pumping ions or protons, transporting molecules across the membrane, facilitating signaling events and more, as described in Section 3.

Carbohydrates

Another important class of biological molecules is carbohydrates or sugars, which have various functions including acting as both chemical fuel storage and structural components. Individual sugar monomers or monosaccharides are identified by their chemical structures. In its open form, each sugar contains one carbonyl group linked to a carbon chain of various lengths, each with a hydroxyl group attached, as seen in the Fischer projection in Figure 5.6. Furthermore, carbohydrates tend to form rings by reaction of the carbonyl group with another carbon atom in the same molecule to form a hemiacetal, as seen in the Haworth projection in Figure 5.6. For aldoses, the carbonyl is on the end of each molecule. If the carbonyl occurs in the middle of the carbon chain, the sugar is called a ketose. The –ose ending in the name of a molecule indicates it is a carbohydrate. A key difference between different sugar types is the chirality of the tetrahedral-bound carbon atoms. In three-dimensional space, the molecular structures of sugars (and in particular their chiral carbons) are not superimposable with their mirror images. While all of the hexoses (six carbon sugars) are isomers with the same chemical formula $C_6H_{12}O_6$, they differ in the spatial arrangement of their chemical bonds.

Nano Fact

Chirality, a property of a molecular structure lacking in symmetry and not superimposable on its mirror image, is very important in the structure of biological molecules such as DNA, protein, and phospholipids. In particular, the monomers of these polymers tend to only exist (or function) in nature as L-amino acids or D-sugars. Several hypotheses have been put forth to provide a mechanism consistent with chemistry, physics, and evolutionary theory, yet there is still no consensus as to why this is the case.

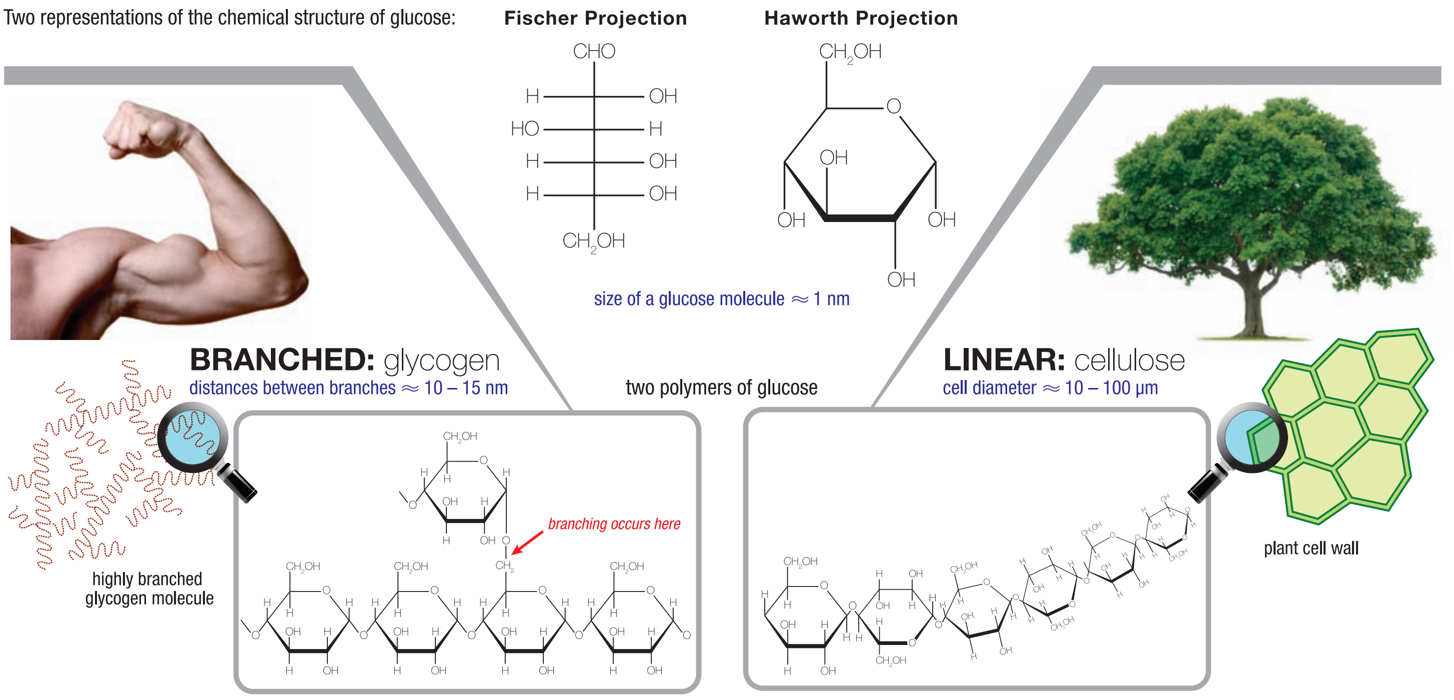


Figure 5.6 Carbohydrates exist as polymers when the individual monomers are linked together to form a chain known as a polysaccharide. Glycogen is a polysaccharide that is a branched structure and is used to store glucose in animals. Cellulose is a polysaccharide that is a linear polymer structure and a large structural component of plants. *See Figure Credits, p. vi.*

Like DNA and proteins, carbohydrates can also exist as polymers when the individual monomers are linked together to form a chain, which is referred to as a polysaccharide. For example, cellulose is a linear polymer of glucose that functions as an important structural component in plants. A difference between polysaccharides and proteins or DNA is that the monomers in polysaccharides can be linked together by a variety of different groups per molecule, whereas the