Chap. 0 General

0.1 Course Description

- This course is intended for graduate students who deal with nanoscience and nanoengineering of organic materials at molecular levels. It covers the nanofabrication tools, different classes of nanostructures, and diverse nanodevices ranging from the electronic, micromechanical, to bio applications.

0.2 Textbooks

1) *Learning Bio-Micro-Nanotechnology* (M. I. Mendelson)
- This book deals with fundamental concepts of micro- and nanotechnology with multidisciplinary applications in electronics, computers, biomedicine, and chemistry. It can be used as a textbook at the college freshman to junior level and designed for students who lack the cross-disciplinary background and knowledge of micro- and nanotechnology

2) *Introduction to Nanoscale Science and Technology* (Ed., M. D. Ventra et. al.)
- This book originated from the courses in nanotechnology at Virginia Tech in spring 2001 and University of Pennsylvania in fall 2002. It has been conceived to provide a broad and through introduction aimed at undergraduate seniors and early graduate students in all of the disciplines ranging from chemistry, physics, electrical and computer engineering, mechanical engineering, chemical engineering, and materials science. The references provided at the end of each chapter will be useful for research in this field.

0.3 Nanoscale Science and Technology

- Defined primarily by a unit of length of the *nanometer* (1 nm = 10^{-9} m).
- The ultimate control over the form and the function of matter at the nanoscale:
  - *Limited by laws of quantum physics.
- Building up of materials and devices with control down to the level of individual atoms and molecules:
  - *Properties and performance far superior to conventional technologies and entirely new phenomena only available at nanoscales.
- Bottom-up approach: putting together smaller components (such as atoms and molecules) to form a larger and more complex system by leveraging naturally occurring chemical, physical, and biological process.
- Emergence of entirely new classes of materials: fullerenes, nanocomposites, quantum dots: the building blocks of completely new structures and devices.

Chap. 1 Thinking Small and Big

1.1 Technology History

- Technology has progressed through the ages by discoveries and inventions of human beings.
  Stone age -> Bronze age -> Industrial age -> Consumer age (Mass production) -> Information age
  -> Genetic age -> *Nanotechnology* age -> Self-assembly age

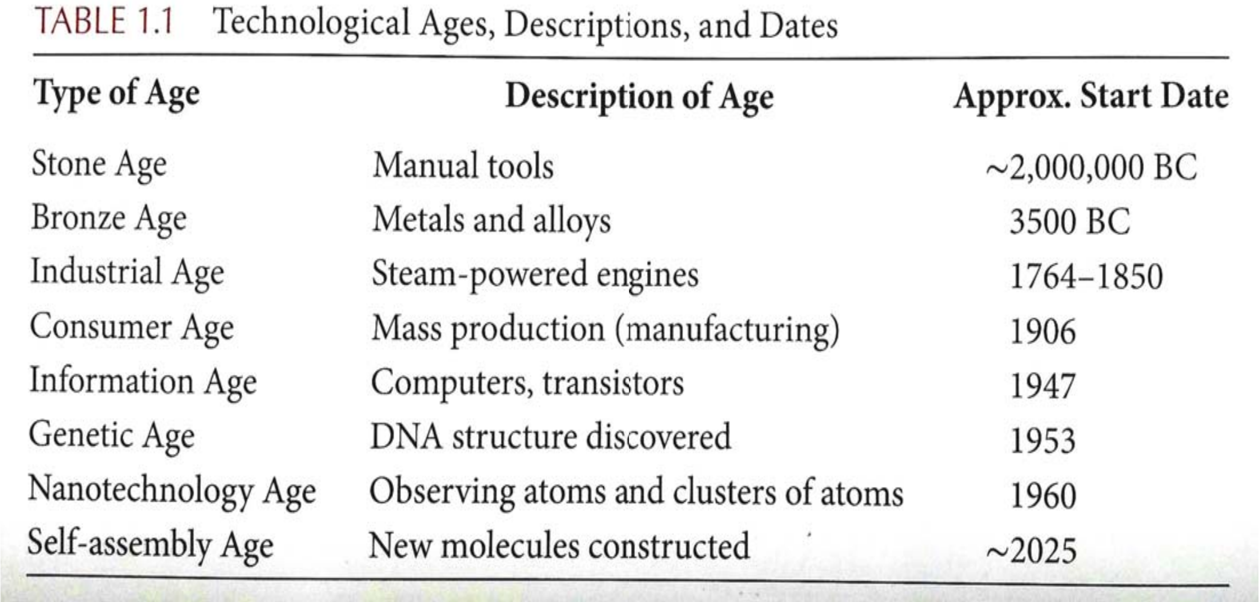


TABLE 1.1 Technological Ages, Descriptions, and Dates

Type of Age	Description of Age	Approx. Start Date
Stone Age	Manual tools	~2,000,000 BC
Bronze Age	Metals and alloys	3500 BC
Industrial Age	Steam-powered engines	1764–1850
Consumer Age	Mass production (manufacturing)	1906
Information Age	Computers, transistors	1947
Genetic Age	DNA structure discovered	1953
Nanotechnology Age	Observing atoms and clusters of atoms	1960
Self-assembly Age	New molecules constructed	~2025

- Stone Age: *Nanotechnology* has been around for centuries, even though people were unaware of it.
  1) Over 5000 years ago, the Egyptians supposedly ingested gold nanoparticles to purify their body and mind.
  2) In the 10th century BC, gold and silver nanoparticles were commonly used in Persia as coloring agents for ceramic pottery.
  3) In the 14th century, nanoparticles were used throughout Europe as coloring agents for stained glass in cathedrals.

- Bronze Age: Around 3500 BC, somebody heated a stone over fire and melted out bronze (an alloy of copper). Soon people were chemically alloying copper with different types of metals like lead, tin, and zinc to make a variety of copper alloys.
  Eventually, iron was processed from iron ore and was alloyed with carbon to form steel.

- Industrial Age and Mass Production (Consumer Age): Invention of the steam engine in 1764.

- Information age: In 1947, the first computer, called ENIAC (Electronic Numerical Integrator and Calculator), was built. It was U-shaped and filled a room-the size of ~25 m(long) by ~6 m (wide)- and used 18,000 vacuum tubes. Also in 1947, the transistor was invented at Bell Lab. The transistor revolutionized computer size, strorage capacity, and data processing.
  The 1st transistor was about 10 mm high. A decade later, the electronics industry was manufacturing microscopic size transistors on silicon chips.
  In 1958, Texas Instruments and Fairchild Semiconductor discovered integrated circuits where many transistors, resistors, and capacitors were simultaneously put on a chip. This led to very large-scale integration (VLSI) in the late 1960s. Today, there are over 500 million transistors in a modern computer.

- Genetic age: In 1953, the discovery of the double helix structure of deoxyribonucleic acid (DNA) was made R. Franklin, J. Watson, and F. Crick.

  DNA holds the genetic information in all living organisms. This genetic information is put into cells through the messenger ribonucleic acid (mRNA). Genetic engineering gives us the ability to modify the genetic code of DNA in order to improve human health.

- *Nanotechnology Age*: At the start of 20th century, quantum physics and chemistry provided the foundation for nanotechnology.
  1) In December 1959, R. Feynman started the nanotechnology revolution in his speech, “There’s Plenty of Room at the Bottom”. He predicted structures would be manufactured from the “bottom-up” - one atom or one molecule at a time.

     Feynman has been called “grandfather of nanotechnology”.
  2) In the early 1970s, a Japanese scientist, Norio Taniguchi, first coined the term “nanotechnology”. However, the terminology did not catch on until the mid-1990s.
  3) R. Smalley (Rice University) discovered “bucky balls” and brought nanotechnology to the forefront of the public awareness. He had to be “father of nanotechnology”.

     We are about to build things that work on the smallest possible length scales – atom-by-atom level of finesse.

- Self-assembly age: The design and arrangements of atoms and molecules into controlled structure.

  -> We should get used to thinking how small molecules will solve big problems.

1.3 Tera-to-Pico Multipliers

- 24 orders of magnitude from tera (10^{12}) down to pico (10^{-12}): size-scale

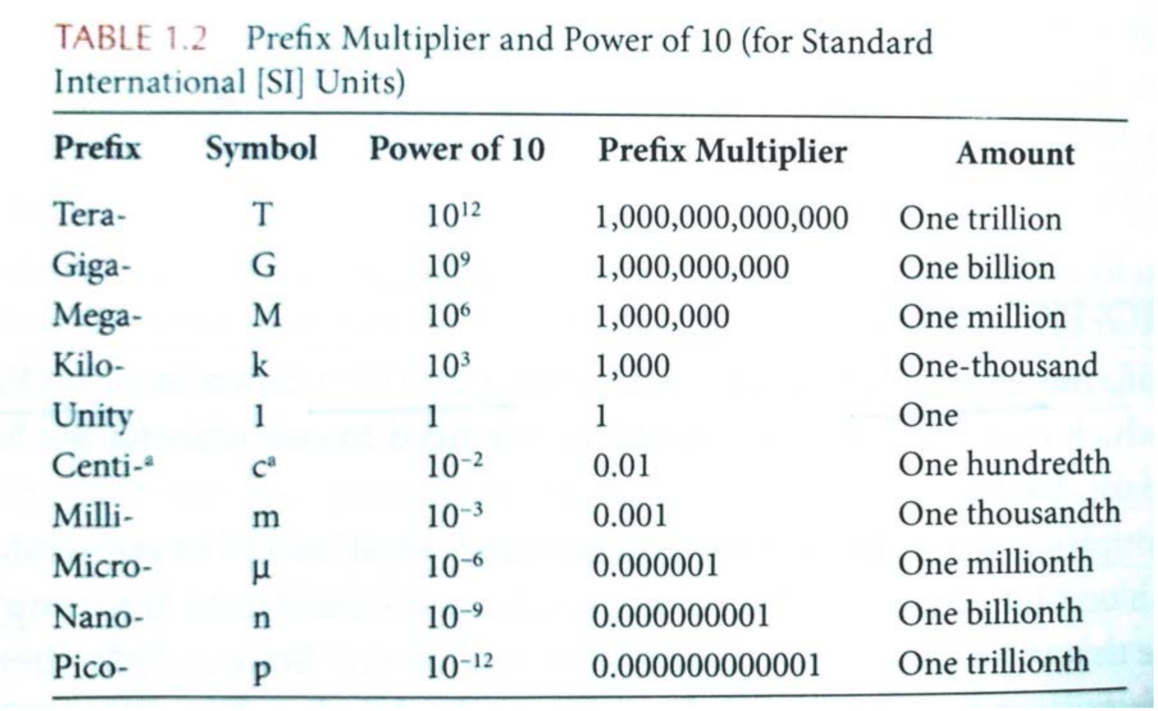


TABLE 1.2 Prefix Multiplier and Power of 10 (for Standard International [SI] Units)

Prefix	Symbol	Power of 10	Prefix Multiplier	Amount
Tera-	T	10^{12}	1,000,000,000,000	One trillion
Giga-	G	10^{9}	1,000,000,000	One billion
Mega-	M	10^{6}	1,000,000	One million
Kilo-	k	10^{3}	1,000	One-thousand
Unity	1	1	1	One
Centi-[a]	c[a]	10^{-2}	0.01	One hundredth
Milli-	m	10^{-3}	0.001	One thousandth
Micro-	µ	10^{-6}	0.000001	One millionth
Nano-	n	10^{-9}	0.000000001	One billionth
Pico-	p	10^{-12}	0.000000000001	One trillionth

1.4 Size of Things

- *Bottom-up* thinking:
  1) Atoms bond together to produce molecules.
  2) Molecules link together to form cells.
  3) Cells join together into tissues that form our organs.
  4) Various organs are integrated into an organ system (digestive system).
  5) All our body’s organ systems connect together to construct our organism.

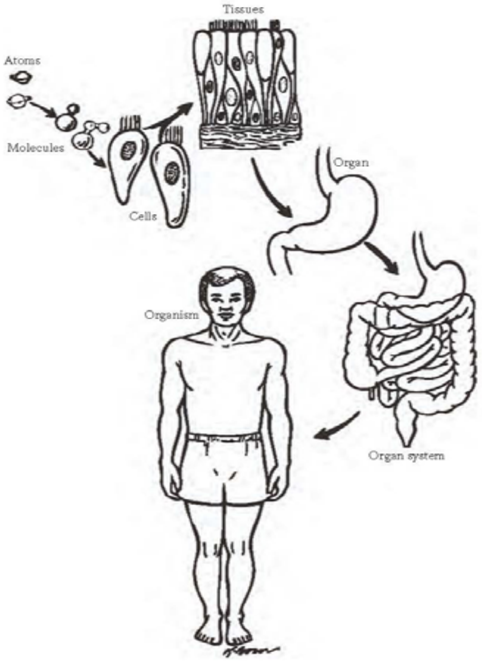


Figure 1.2 Illustration of features in the human body from smallest (atoms) to largest (human) and vice versa.

- *Top-down* thinking:
    1) A person is 1.8 m tall in the macroscopic world.
    2) When the organism is reduced 1000 times, it would be the size of body tissues (~ mm).
    3) When reduced another 1000 times, it would be the size of cells (~ um).
    4) Reducing it another 1000 times, it would put you into nanometer (molecular) size.

- The common size of features in nature and those that are man-made: *natural* vs *synthetic*

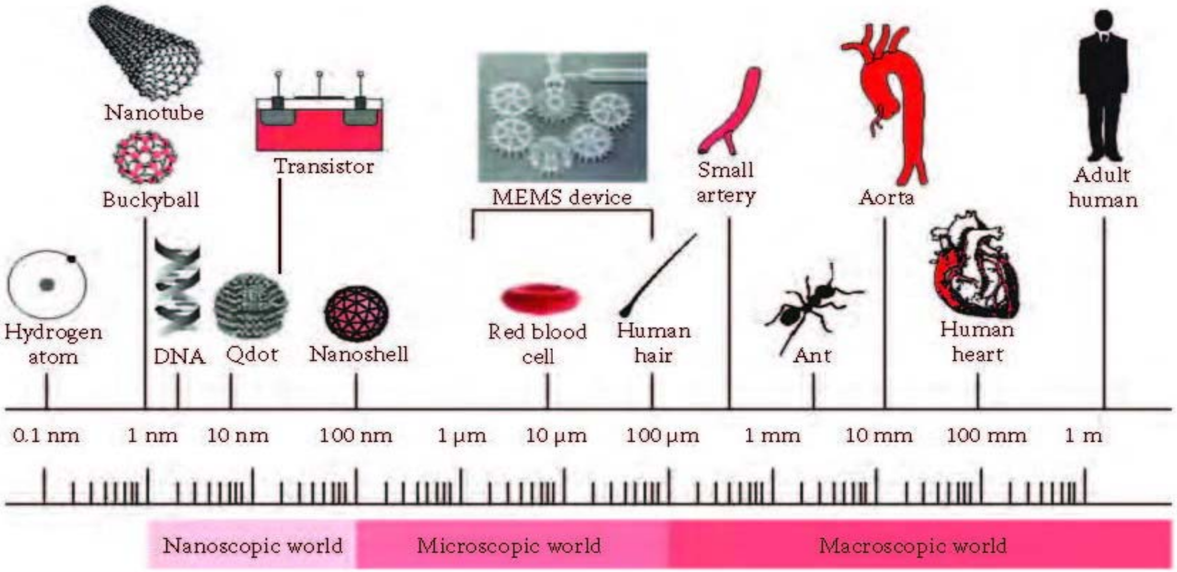


Figure 1.3 Illustration of the size of things in nature for the nanoscopic, microscopic, and macroscopic worlds. Sizes increase in going left to right: 0.1 nm ⊠1 m. The size of the features is approximate. MEMS, microelectromechanical systems; Qdot, quantum dot.

- Macroscopic world: The size above which can be resolved with the naked eye.
  The unaided eye can see down to slightly less than 100 um (diameter of a human hair).
  *100 um: the lower limit of the macroscopic world and the upper limit of the microscopic world.
- Microscopic world: the size range we can solve with an optical (light) microscope.
  Typically in the range of ~ 0.1 – 100 um: cells, capillary blood vessels, bacteria, MEMS.
- Nanoscopic world: the size range from 1 to 100 nm (molecules - like DNA, proteins, nanotubes, viruses, transistors), resolved with an electron microscope or atomic force microscope.

1.5 What's Small Technology?

- "Nano" comes from the Greek word "dwarf".
- "Top-down" vs "Bottom-up" manufacturing

Figure 1.5 Cartoon showing a sculptor chipping away stone by "top-down" manufacturing to form a 22 nm size "N" in the NANO-structure. This is called top-down fabrication. [Adapted from von Oech, R., *A Whack on the Side of the Head*, 3rd edn., p. 124, Warner Books, Inc., New York, 1998.]

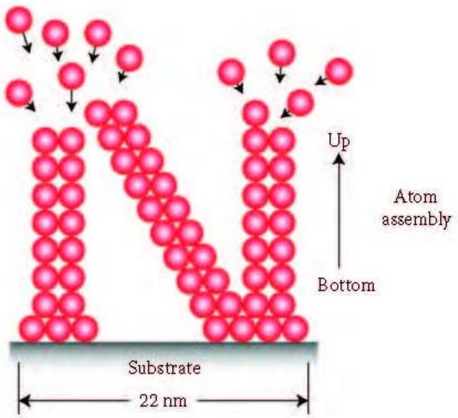


Figure 1.6 Illustration of "bottom-up" manufacturing to form the 22 nm size "N" in NANO.

- Definition of “small” into “micro” and “nano”

  Microtechnology refers to microdevices (>100 nm) - like integrated circuits on a chip and MEMS. (In most cases, synthetic materials such as silicon, glass, and plastics are used and fabricated from “*top-down*”)

  Nanotechnology covers the size range of 1-100 nm where at least one dimension in the structure has a size of < ~100 nm. DNA molecules have lengths exceeding 100 nm, but the diameter of the double helix is ~2.1 nm. Nanostructures have novel chemical and physical properties such as different kinds of molecular interactions, electrical conductivity, and strength over macroscopic structures. These nanostructures are manufactured from “*bottom-up*”.

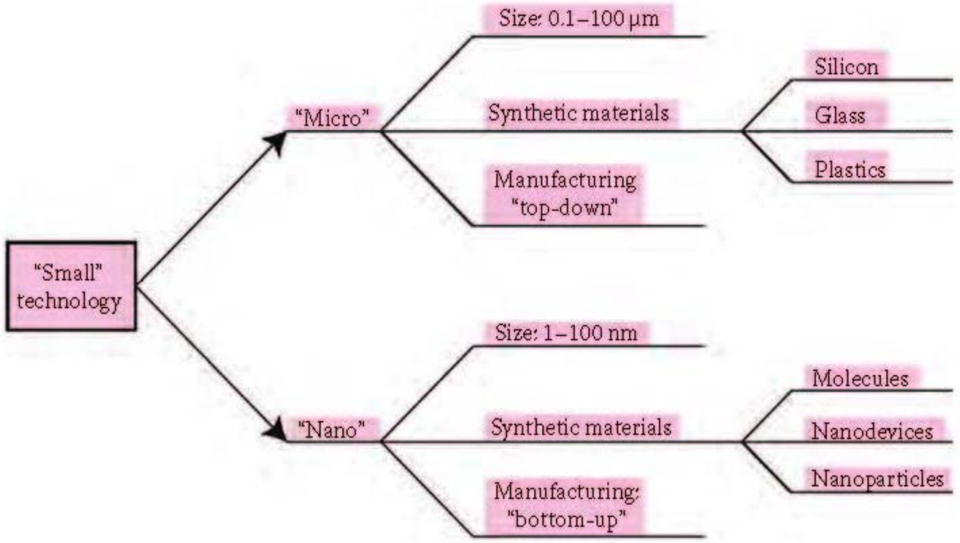


Figure 1.7 Tree diagram classifying the definition of “small” into “micro” and “nano.” The diagram shows the difference between “micro” and “nano” depends upon size, material, and manufacturing method.

*DNA molecule and AFM image of 2D architecture of DNA origami.

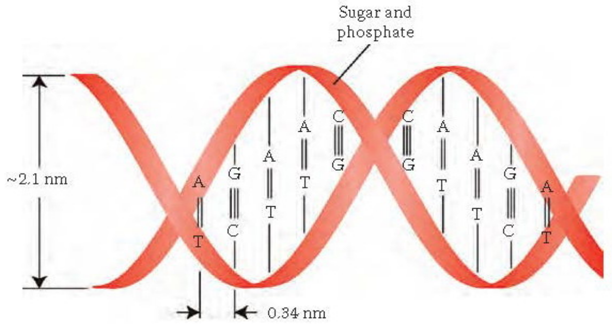
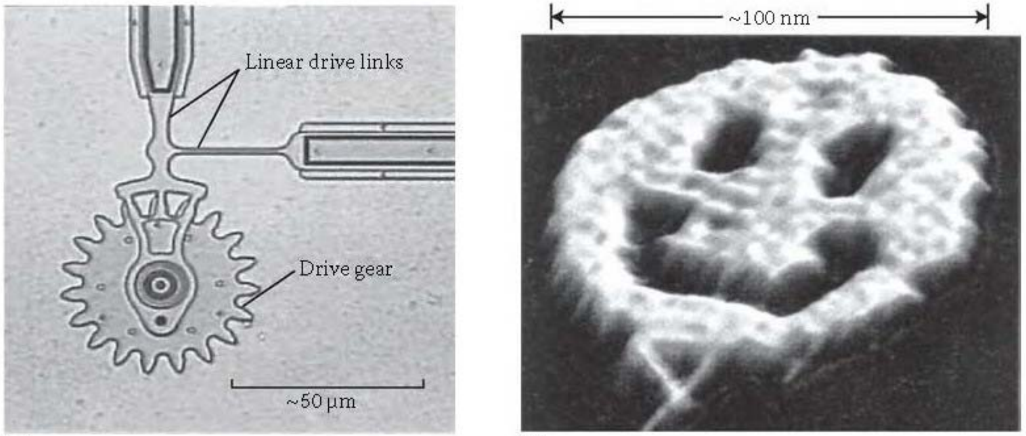


Figure 1.9 Illustration of DNA molecule with approximate dimensions of the helix diameter and base-pair spacing.



(a)

(b)

Figure 1.8 Micrographs of (a) MEMS drive gear and links. [Courtesy of Sandia National Laboratories, Albuquerque, NM.] (b) Atomic force microscope image of 2-D architecture of DNA origami. [From Rothemund, P.W.K., *Nature*, 440, 297, 2006. With permission.]

- Physically speaking, how large is 1 nm?
  Atoms in the Periodic Table have an average diameter of about 0.2 nm. If we stack 5 silicon atoms side by side, their total length will be ~1 nm.

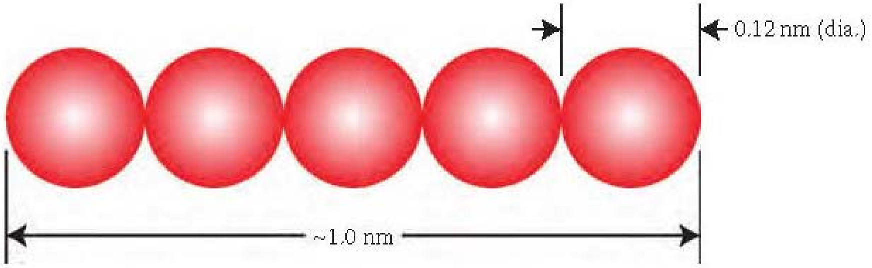


Figure 1.10 Illustration of five silicon (Si) atoms stacked together side by side, which gives a length of approximately 1 nm.

- Is smaller better?
  Smaller sizes have more functionality per unit area (like lap-on-a-chip) because they are more chemically reactive, faster, use less energy, and can store more data in computers.
  However, they may not be necessarily better due to the environmental, health, and safety risks.

1.6 Memory Lane in Electronics

- *Moore's law* : how the number of transistors on a chip would increase with time
  (*empirical* relationship, not a physical law of nature)
  1) The number of transistors on a chip would double every 18-24 months.
  2) In 1985, the transistor size was 1 um and the transistor density (number of transistors per chip area) was 1 million(M)/mm^2.
  3) In 2008, the transistor size had shrunk to ~45 nm and the density increased to 400 M/mm^2. (400-fold increase in density in 23 years)

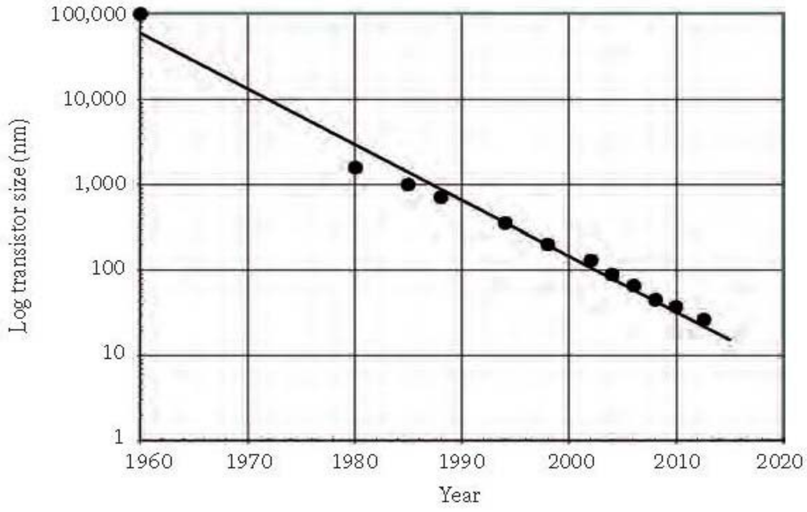


Figure 1.11 Plot of transistor size (log scale) vs. time (1960–2008). Least-squares line. Table of a
data were taken from Hansen, G.W., *Fundamentals of Nanoelectronics*, Pearson Prentice Hall, Upper
2008.]

1.7 Merging The Disciplines

- Education *without boarders*: Nature does not have disciplinary boundaries.
  1) Small technology involves merging the life sciences together with the physical sciences and engineering.
  2) There is an overlap of biology, chemistry, physics, and engineering, along with their subdisciplines.

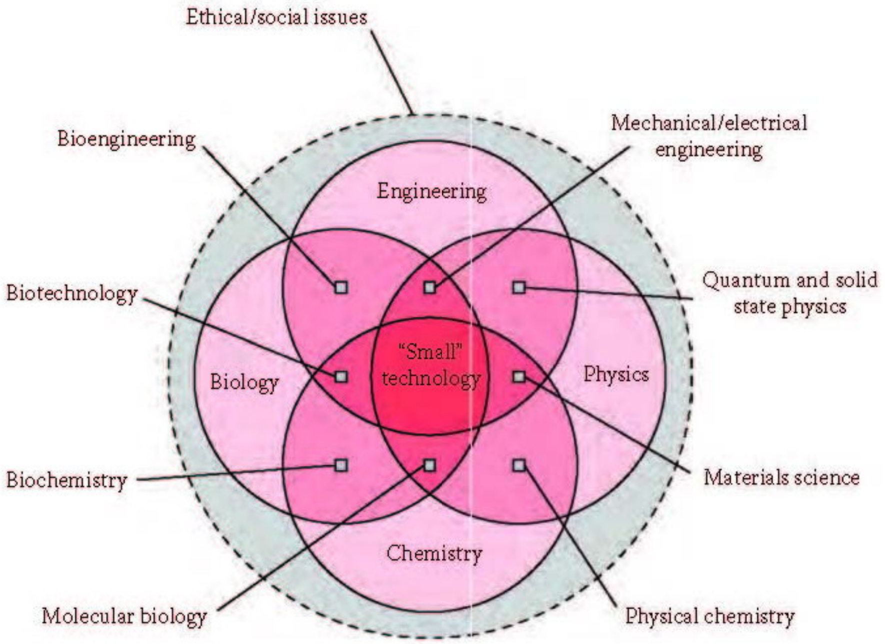


Figure 1.12 Venn diagram showing the cross-disciplinary nature of "small" technology. Ethics/social issues overlap all the disciplines. And the disciplines of biology, engineering, physics, and chemistry overlap each other with the subdisciplines indicated.

1.8 Applications and Implications of Nanotechnology

1) **Health and longevity**: sensors, actuators, biomedical devices, and drurgs / nanoshells and targeted agents for cancer therapy / portable microfluidic devices for genetic diagnostics and early detection of disease / nanoparticles and biomolecules delivering drugs to cells / longer-lasting power sources for implanted devices / better biomaterials for repairing and replacing organs, joints, and arteries / important anti-viral drugs and strengthened immune systems / fast, accurate, and inexpensive DNA analysis.

2) **Electronics and information technology**: smaller ICs on-a-chip, faster computers, increased memory / quantum bits to store more data in smaller computers / fast data processing with photonics (laser-on-a-chip) / wireleee cell phones with long battery life.

3) **Energy**: Harnessing the energy of molecular motors in the mitochondria of our cells / lightweight, high-strength composites improving energy efficiency in transportation vehicles / low-cost LEDs and quantum dots for lighting, display, and imaging systems / piezoelectric nanowires that convert mechanical energy into electrical energy / longer lasting micro/nano-batteries / improved efficiency, lower cost solar cells, and high power-density fuel cells.

4) **Transportation and security**: smaller, higher sensitivity sensors for airport security, bombs, and biological weapons / improved artificial intelligence for macro-, micro-, and nano-robots / stronger, lighter-weight composite materials for use in space vehicles, airframes, automobiles, buildings, bridges.

- Applications in human body: microsensors, microactuators, biomedical devices
  A sensor “senses” and “detects” the presence of something – like certain chemicals, toxins, or proteins. An actuator is a device which “acts” or simply “takes action”

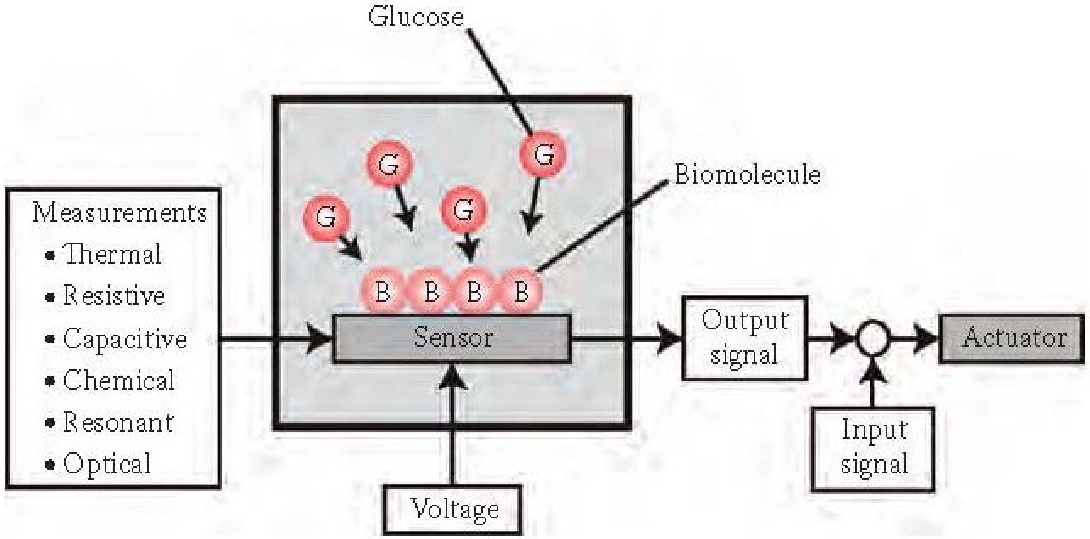


Figure 1.13 Schematic illustration of a sensor that has an output signal that is compared to a set point. The difference is fed to an actuator. The illustration shows a signal detecting the binding of glucose molecules to biomolecules. The signal is compared to a set point (input signal) and the difference is sent to an actuator. Some of the types of sensor measurements are shown.

Biomedical microsensors and microactuators: angioplasty sensors, blood pressure sensors, catheter sensors, glucose watch, heartbeat sensors, inhaler micro-pumps, prosthetic leg sensors, etc.

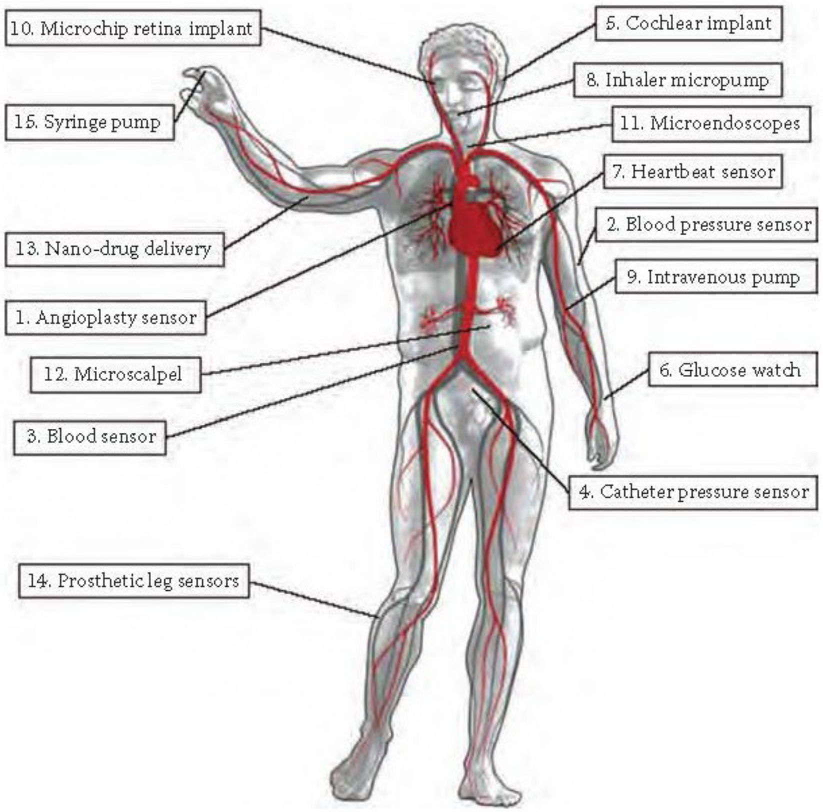


Figure 1.14 Applications of different types of microdevices that can be used to monitor and control the various functions in the human body. [Adapted from Wikimedia Commons.]

- Micro-Examples: microfluidics, microarrays

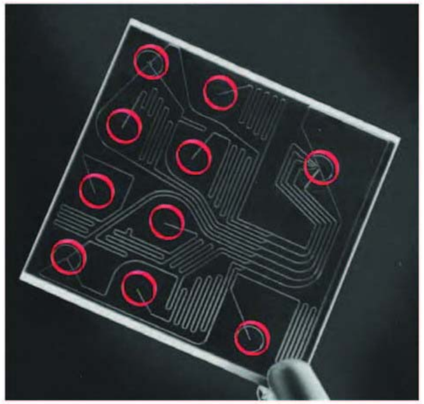


Figure 1.16 Photograph of a microfluidic device, showing channels and circular ports. Smal
ids flow through the microchannels that are analyzed. [Courtesy of Agilent Technologies, Santa

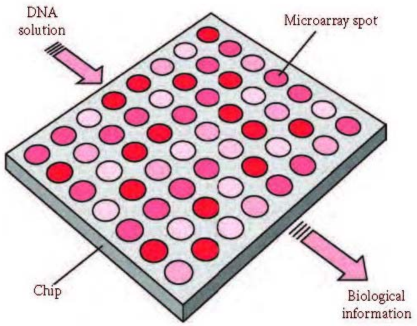


Figure 1.17 Schematic illustration of a microarray, showing a chip (made of glass, silicon, or plastic) with an ar
of different colored micro-spots. Microarrays are color sensors that are used to analyze genetic data.

- Nano-Examples: molecules (fullerine, CNT), nanodevices (FET, nanowire), nanoparticles/nanoshells

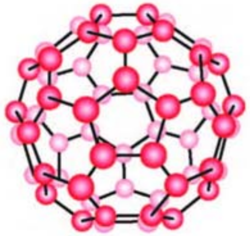


Figure 1.18 Illustration of a buckyball that is a molecule made up of carbon atoms. The atoms are
the form of a soccer ball.

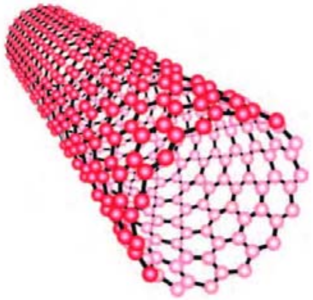


Figure 1.19 Illustration of single-walled nanotube. The nanotube is a molecule that consists of a single laye
carbon atoms in the shape of a cylinder.

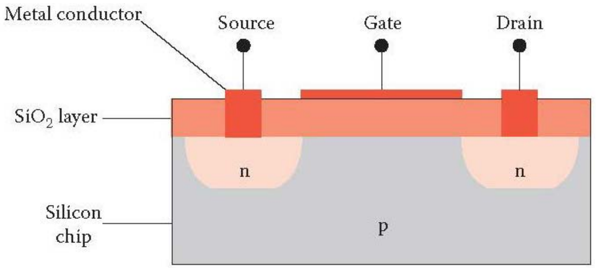


Figure 1.20 Cross-sectional illustration of a field-effect transistor (FET) on a silicon chip, p-type semiconductors, SiO$_2$ layer, and metal conductor pads (source, gate, and drain).

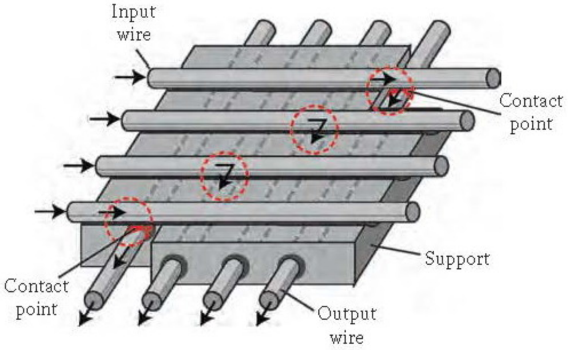


Figure 1.21 Illustration of perpendicular arrays with a molecular layer (support) that is sand top array (input) and bottom array (output).

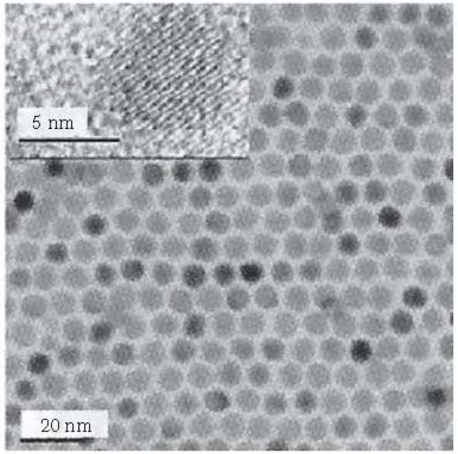


Figure 1.22 Micrograph of dried colloidal solution of ~5 nm diameter size CdSe Qdots. *Mater. Matters*, 2 (1), 10, 2007. With permission.]

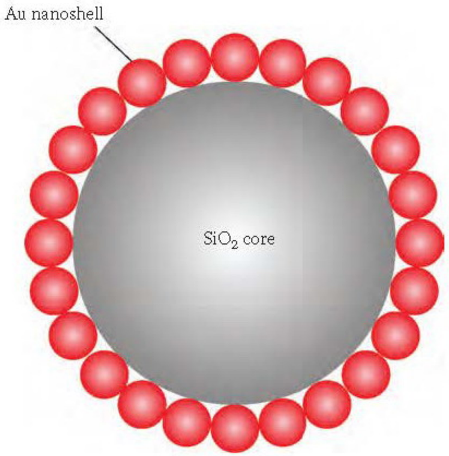
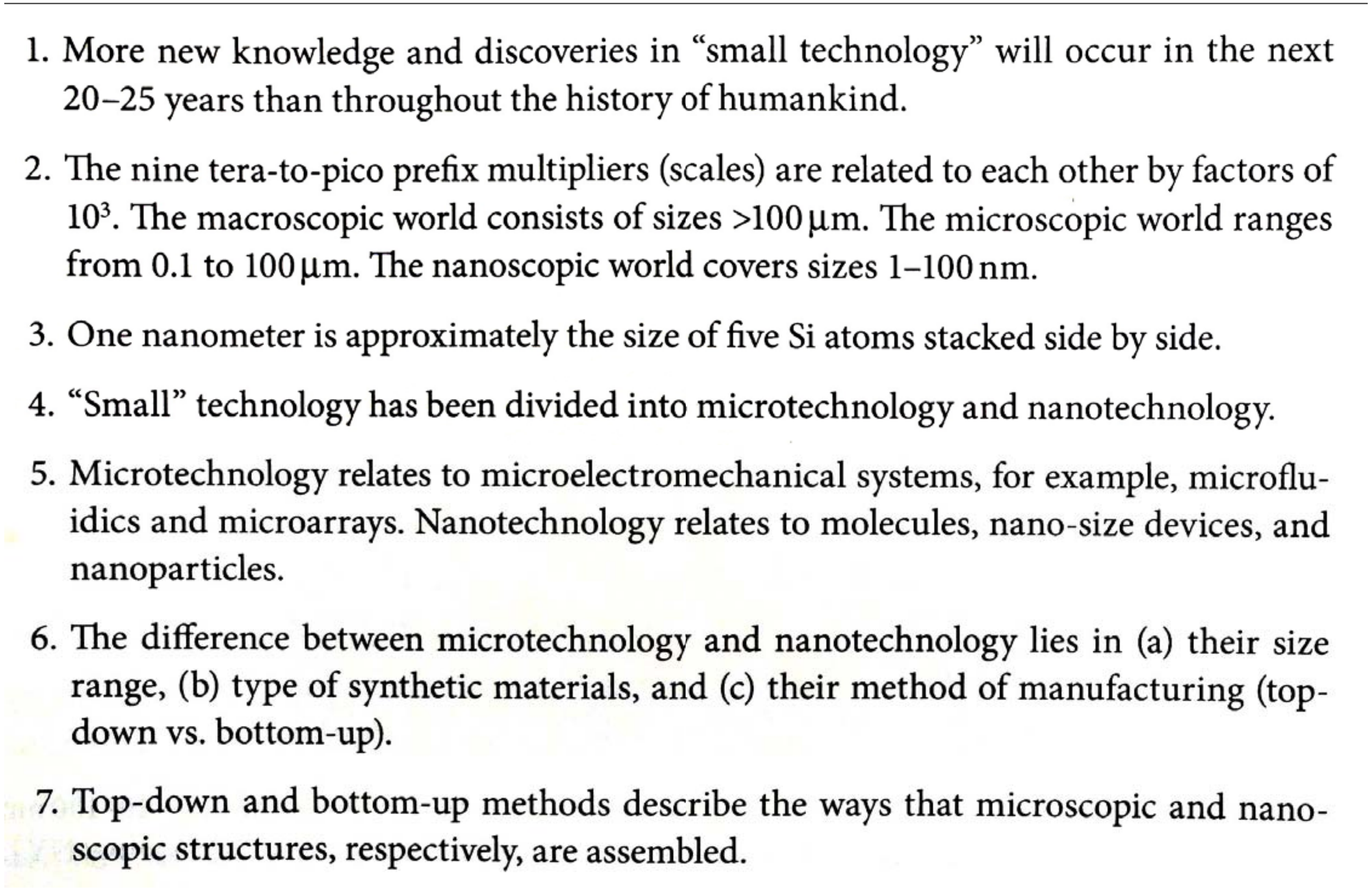
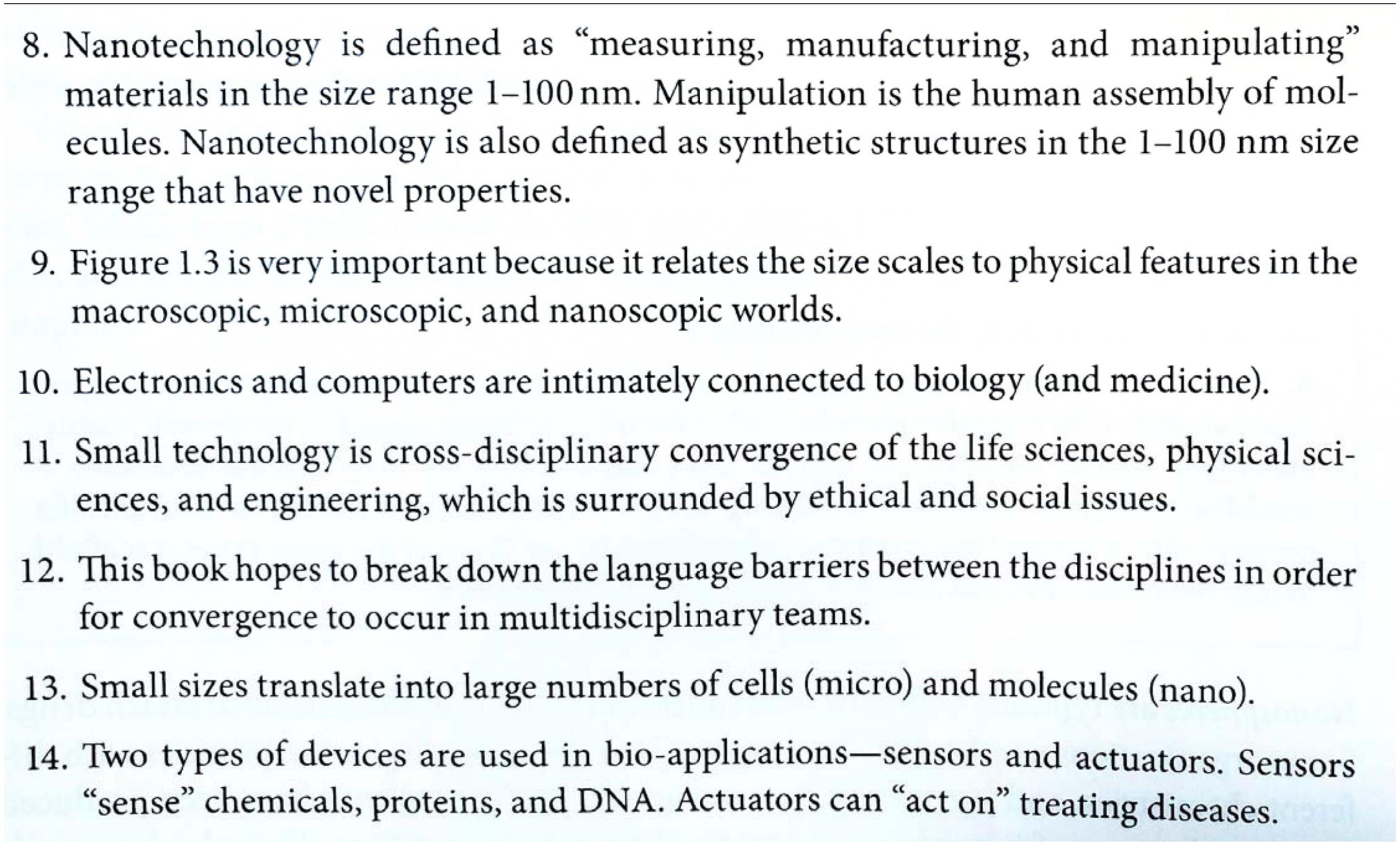


Figure 1.23 Illustration of a nanoshell gold (Au) coating on SiO$_2$ core. Gold nanoparticles to the core.

1.9 Key Concepts



1. More new knowledge and discoveries in "small technology" will occur in the next 20–25 years than throughout the history of humankind.
2. The nine tera-to-pico prefix multipliers (scales) are related to each other by factors of 10^3. The macroscopic world consists of sizes >100 µm. The microscopic world ranges from 0.1 to 100 µm. The nanoscopic world covers sizes 1–100 nm.
3. One nanometer is approximately the size of five Si atoms stacked side by side.
4. "Small" technology has been divided into microtechnology and nanotechnology.
5. Microtechnology relates to microelectromechanical systems, for example, microfluidics and microarrays. Nanotechnology relates to molecules, nano-size devices, and nanoparticles.
6. The difference between microtechnology and nanotechnology lies in (a) their size range, (b) type of synthetic materials, and (c) their method of manufacturing (top-down vs. bottom-up).
7. Top-down and bottom-up methods describe the ways that microscopic and nanoscopic structures, respectively, are assembled.



8. Nanotechnology is defined as "measuring, manufacturing, and manipulating" materials in the size range 1–100 nm. Manipulation is the human assembly of molecules. Nanotechnology is also defined as synthetic structures in the 1–100 nm size range that have novel properties.

9. Figure 1.3 is very important because it relates the size scales to physical features in the macroscopic, microscopic, and nanoscopic worlds.

10. Electronics and computers are intimately connected to biology (and medicine).

11. Small technology is cross-disciplinary convergence of the life sciences, physical sciences, and engineering, which is surrounded by ethical and social issues.

12. This book hopes to break down the language barriers between the disciplines in order for convergence to occur in multidisciplinary teams.

13. Small sizes translate into large numbers of cells (micro) and molecules (nano).

14. Two types of devices are used in bio-applications—sensors and actuators. Sensors "sense" chemicals, proteins, and DNA. Actuators can "act on" treating diseases.

[Homework/Reading Assignment]

1. Aldaye, F. et. al, Molecular architecture using DNA, *Science*, 321, 1795 (2008).
2. Rothemund, P.W.K., DNA origami, Nature, 440, 297 (2006).