Chap. 4 Bit of Physics

4.1 Introduction

- Failure of classical (Newtonian) mechanics: black-body radiation, harmonic oscillation, atomic emission spectra, the dual nature of light -> quantum theory or wave mechanics.
- *Very small* masses and sizes (down below the nano-level): average size of an atom ~0.2 nm. The mass of an electron, 9.1×10^{-31} kg, the mass of a proton, 1.6×10^{-27} kg.

*R. Feynman: At the atomic level, we have new kinds of forces, new kinds of possibilities and new kinds of effects.

4.2 Size Matters

- Feynman referred to a range of technologies that were thousands of times smaller than the nanotechnology; picotechnology (one-trillionth, 10^{-12}m) and femtotechnology (one-quadrillionth, 10^{-15}m).
- The nanoscopic range is at the molecular level, the pico range is at or below the atomic level, and the femto range is around the range of uncertainty for an electron.

[Question] What happens to the physical laws of nature when the size gets smaller and smaller?

- We enter into a new regime where the effects of surface and atomic interactions become more important than mass or volume in influencing the physical properties of matter.

4.3 Working Toward The Bottom

4.3.1 Starting at the Top

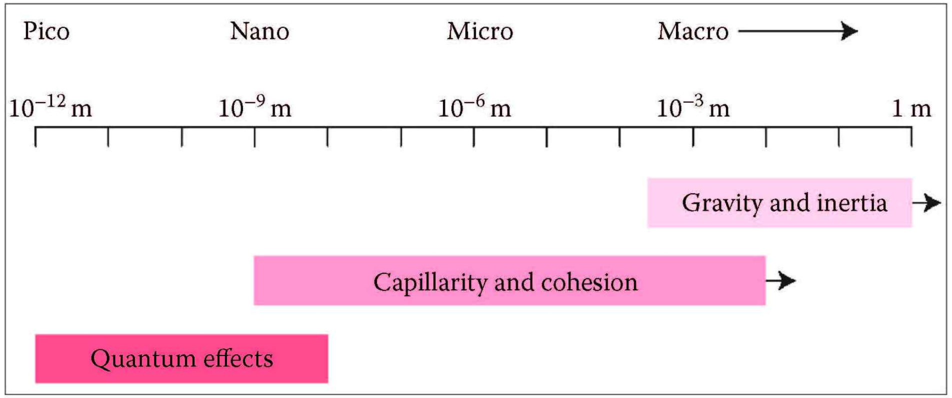
- Classical physics (mechanics): In the 17th century, Sir I. Newton created the laws of gravity and inertia.
  Gravity is "a force of attraction that massive objects exert on each other".
  The law of inertia is defined in a way that "a body at rest will remain at rest, and a body moving at a constant velocity will continue to do so (unless disturbed by an outside force)"
  When starting at the top, we are dealing with Newton's gravity and inertia.

*Newton considered macroscopic objects, not atoms or molecules (which are neither massive nor stationary).

*Feynman once said "All things are made up of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, and repelling each other when they are squeezed into one another".

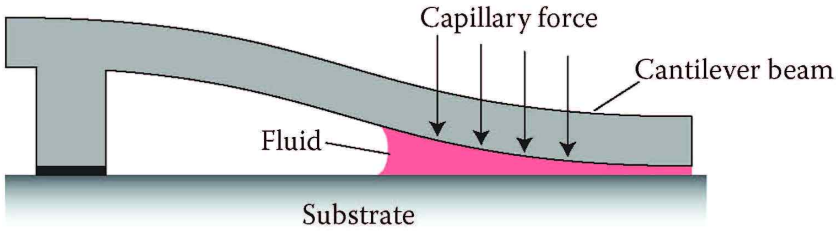
[Question] How small is small for classical mechanics to fail?

- The approximate size regimes where different laws of physics apply – gravity and inertia, capillarity and cohesion (surface effects), and quantum effects.



1.3 Different size ranges being dominated by different physical laws.

- In the microscopic range, the capillary force of a liquid pulls the unsupported end of a micro-cantilever beam toward the substrate.



Cantilever beam of MEMS device acted on by capillary force pulling it toward substrate.

- As the size is reduced, the surface effects can create major problems:
  "If God created solids, the devil created surfaces."

- In the *nanoscopic* world,
  1) capillarity and cohesion will still exist to the molecular level.
  2) however, at the molecular level (1 – 100 nm), intermolecular forces such as dipole-dipole interactions play a dominant role.
  3) at the atomic level, we will start entering a new regime where the quantum effects will dominate. Quantum mechanics involves electrons behaving as waves, being able to tunnel through barriers, and existing in discreet energy levels in atoms.

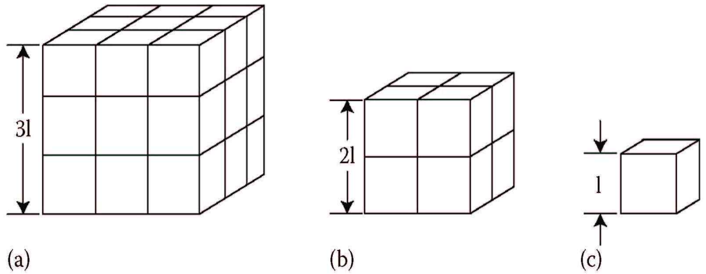
4.3.2 Surface Effects:

- Surface area-to-volume, surface tension, molecular adhesion and cohesion, surface physics of liquids, surface physics of solids

1) Surface area-to-volume

- The surface area affects such engineering parameters as pressure, flow rate (in fluid mechanics), and chemical reactivity.
- Small particles are characterized in terms of their surface area-to-volume ratio (S_v), which correlates very well with the geometrical size of small things.
  Higher surface/volume explains why small apples ripen faster than larger apples, and small ice cubes melt faster than large ice cubes.

- What is the surface area-to-volume ratio of the cubes?

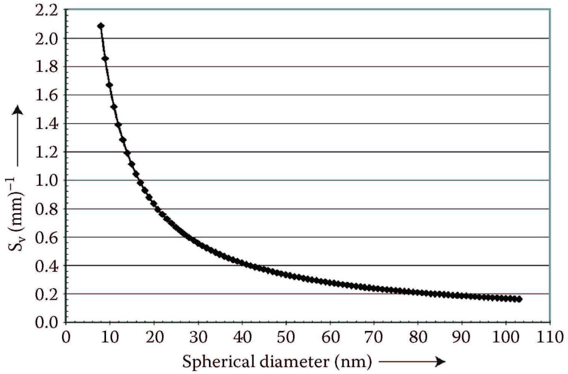


Three different size cubes of edge length (a) 3l, (b) 2l, and (c) l. [Adapted from McMahon,

$$S = 54l^2,\ 24l^2,\ 6l^2;\ V = 27l^3,\ 8l^3,\ l^3.$$

-> $S_v = 2/l,\ 3/l,\ 6/l$ as the cube size decreases.

- For a spherical particle with diameter D, $S_v = 6/D$.



Graph of surface-to-volume ratio (S_V) vs. diameter (nm) for a spherical nanoparticle.

2) Surface tension

- Surface tension is defined as the force per unit length or the line tension that the environment exerts on a surface to minimize its exposed area.
  There is a boundary between a liquid and another medium (say, ambient air). The boundary is acted upon by a surface force that tends to contract the liquid to minimize its surface.
  -> Liquids (water, soap bubbles, and oil) will all contract into spherical droplets in order to minimize their exposed area due to surface forces acting on them.

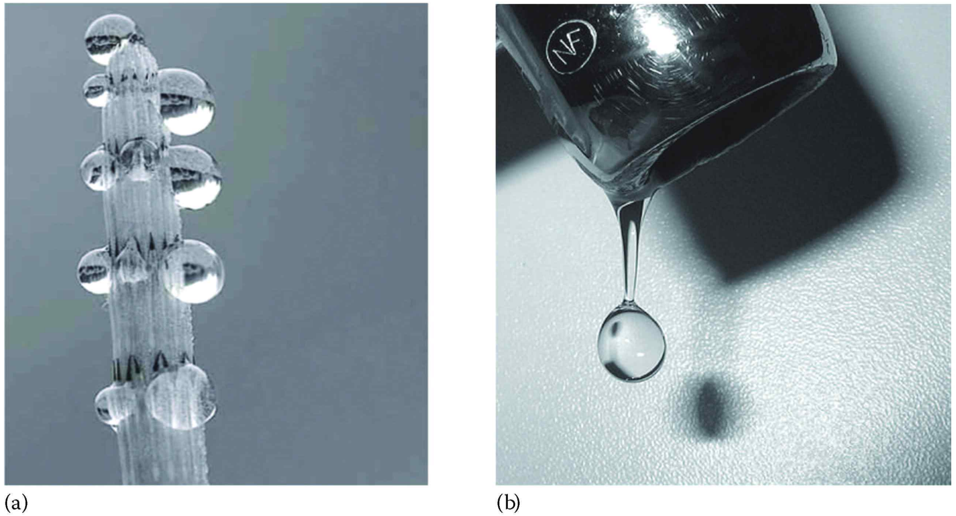

(a) (b)

Figure 4.9 Photographs of (a) water droplets on blades of grass. [Courtesy of Staffan Enborn, originally po
Flickr.] (b) Water droplet detaching from a faucet. [Courtesy of Roger McLassus.]

- Water sliders (insects) on water.
  The surface tension of water (F_S) and the buoyancy force (F_B) exert upward forces exceed to support the downward force of the insect weight (F_G), i.e., $F_G < F_S + F_B$.

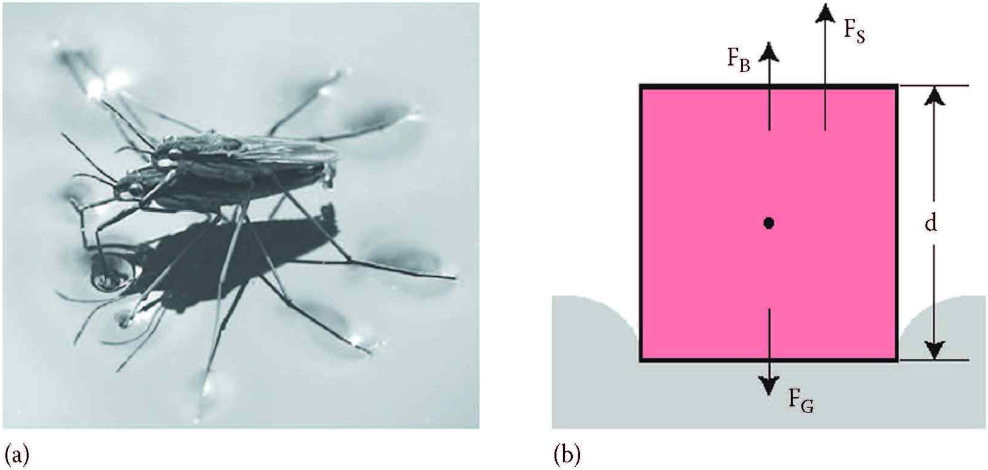


Figure 4.10 (a) Photograph of two water striders mating on water. [Courtesy of Markus Gayda.] (b) The characteristic dimension (d) of a cube at which surface tension of water becomes important. [Courtesy of Sandia National Laboratories, Albuquerque, NM.]

3) Molecular adhesion and cohesion

- Adhesion is the sticky attraction of the liquid molecules to "unlike" molecules – like liquids being attracted to the wall of a drinking cup. Here, the capillary forces act on the liquid and the capillarity is another word for adhesion.

- Cohesion refers to the sticky interaction of “like” molecules for each other. The molecules will stick together due to molecular attraction. Cohesion occurs by dipole-dipole (van der Waals) forces acting on them.
- In liquids, the surface tension is related to the adhesive and cohesive forces of its surrounding molecules. There is a balance of forces between the adhesion of the container wall acting on the top molecules and the cohesion of the neighboring molecules.

-> The result is the formation of a meniscus due to capillary forces.

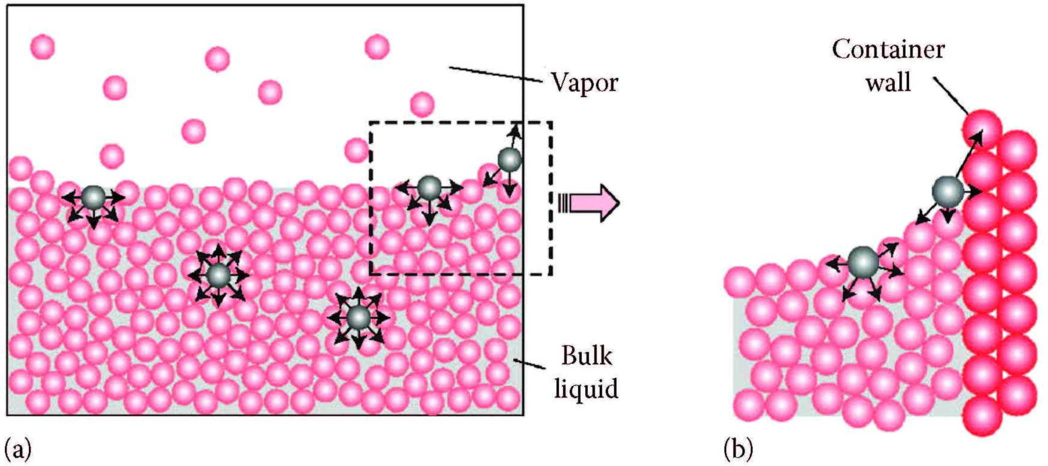
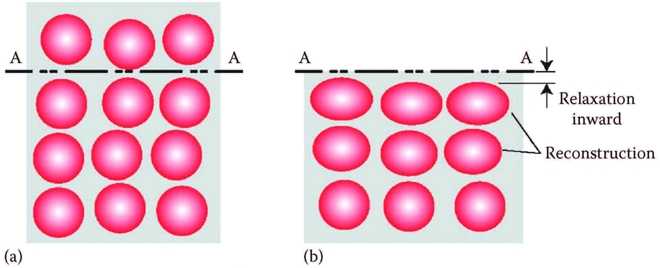


Figure 4.11 Illustration of forces acting on (a) liquid molecules in container. [Adapted from Moore, W.J., *Physical Chemistry*, 2nd edn., p. 498, Prentice Hall, Englewood Cliffs, NJ, 1960.] and (b) enlarged view of molecules at container wall.

4) Surface physics of liquid and solid

- Relaxation and reconstruction of surface and surface molecules/atoms.
  In liquids, the surface molecules are very mobile and can easily rearranged themselves.
  In solids, the atoms are very immobile and the chemical bonding is weaker at the surfaces of solids -> The surface atoms bulge outward – exactly opposite of what happens in liquid surfaces.



Cleavage of liquid molecules

Figure 4.12 Illustration of (a) layer of liquid molecules that is cleaved along plane A–A, and (b) the top layer is stripped away, which exposes the surface of the bottom layer. Molecules (red balls) near the surface undergo inward relaxation and reconstruction.

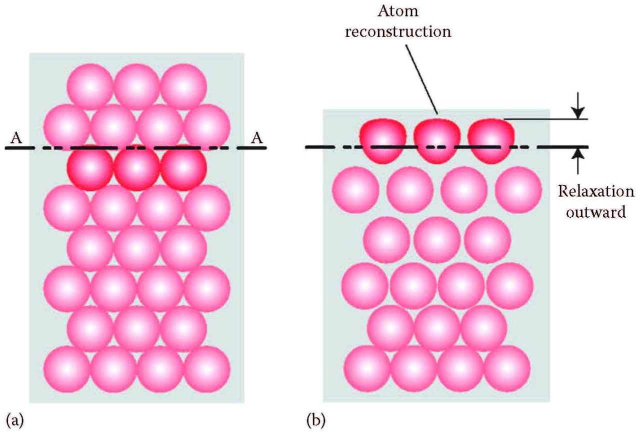
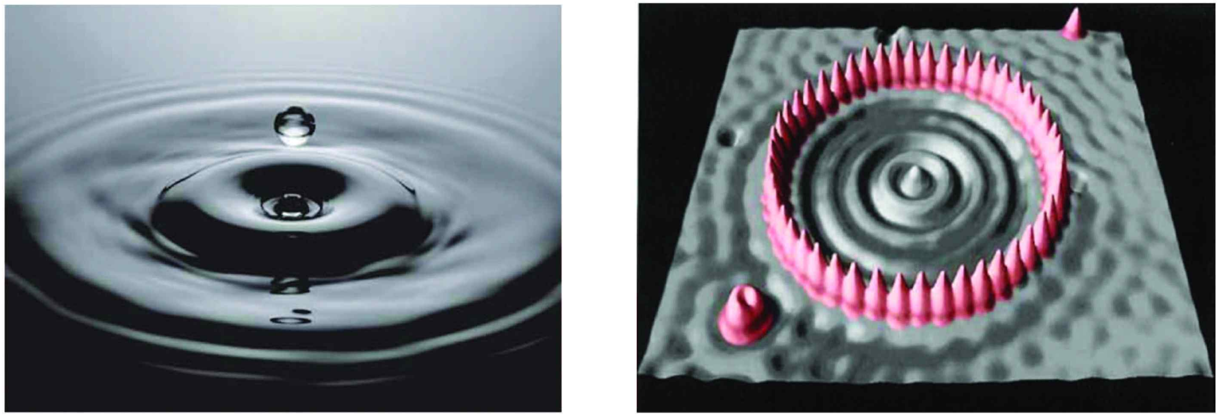


Figure 4.13 Illustration of (a) layer of atoms that is cleaved along plane A–A, and (b) the top layer is stripped away, which exposes surface to outward relaxation and reconstruction.

4.4 Definitions at The Bottom

4.4.1 What are Waves?

- Waves can be defined as a displacement, disturbance, or energy that moves in a sinusoidal path through space;



(a)

(b)

Figure 4.14 Images of (a) wave pattern of water after a droplet has hit the water's surface [Courtesy of Roger McLassus.] and (b) electron wave image of iron atoms on copper. [From IBM Almaden Research Center. With permission.] Illustrations relate the macroworld of waves to the nanoworld of waves.

- The motion of a sinusoidal wave: $y = A\sin\left(\frac{2\pi ct}{\lambda}\right)$

4.4.2 Electromagnetic Spectrum

- Electromagnetic waves propagate as two interconnecting electrical and magnetic vectors in orthogonal directions.

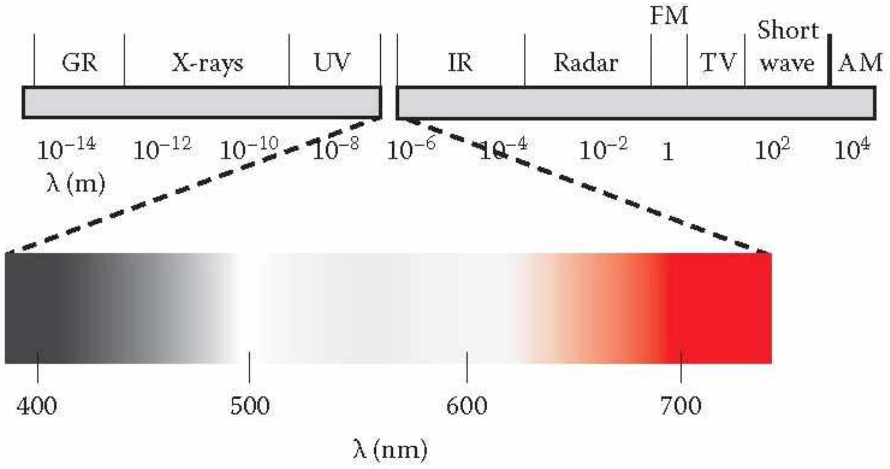
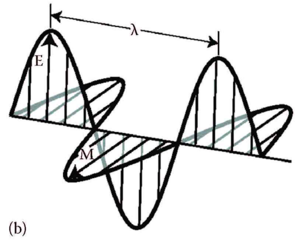


Figure 4.16 Electromagnetic (EM) spectrum. Gamma rays (GR) at left to radio waves (AM) at right, shown in meters for wavelength (λ). Visible spectrum shown between 400 and 700 nm. UV = ultraviolet; IR = infrared. [Adapted from Kaiser, P.K., *The Joy of Visual Perception: A Web Book*, York University, Toronto, Ontario, Canada, 1996–2009. http://www.yorku.ca/eye/thejoy.htm]



4.4.8 Bohr Atom

- A model of the atom that consisted of concentric circles to indicate different electron shells around the nucleus.

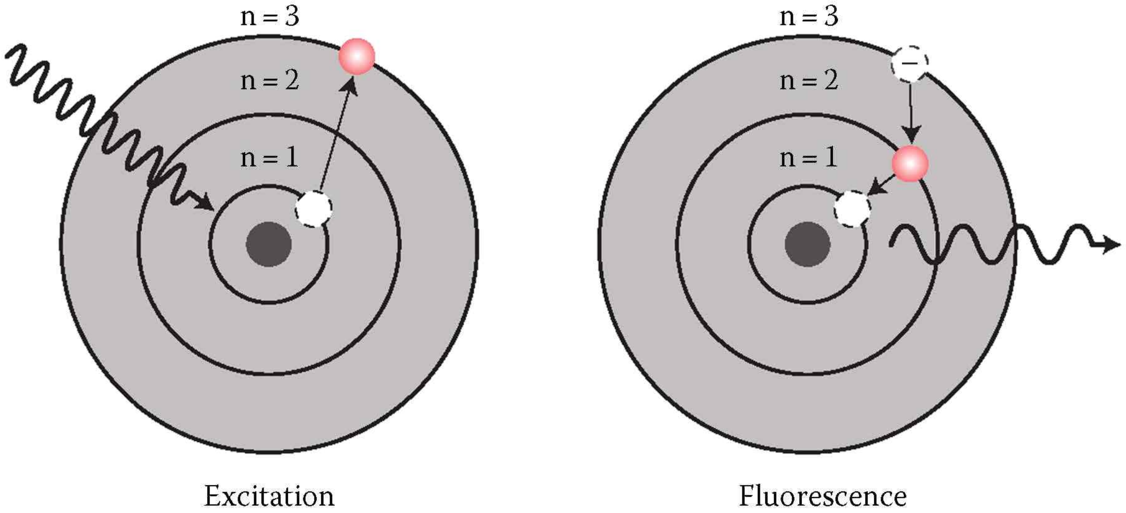


Figure 4.22 Illustration of fluorescence, which is modeled by the Bohr atom, where n = principal quantum number. Incoming radiation excites an electron to a higher energy state, which emits fluorescence when the electron returns to its original state.

4.4.10 Quantum Mechanics

- Quantization: A discrete number of wavelengths ($n\lambda$) are equal to the circumference of the orbital ($2\pi R$) in the Bohr atom.

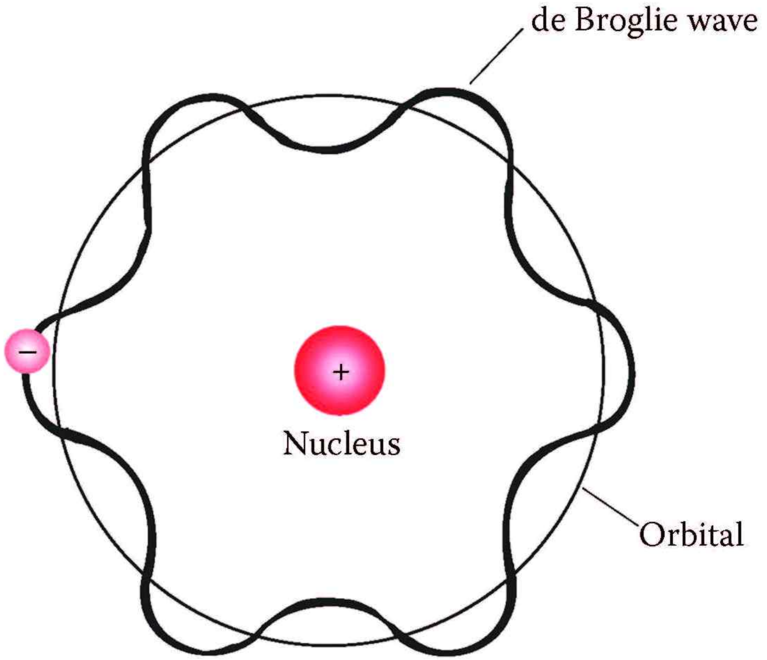


Illustration of de Broglie electron wave encircling the nucleus. The radius (R)

4.5 Energy Levels and Bonding

4.5.1 Particle in a Potential Well

- The electrons can have both particle and wave characteristics. Potential wells are used to determine the density of electron energy levels in atoms.

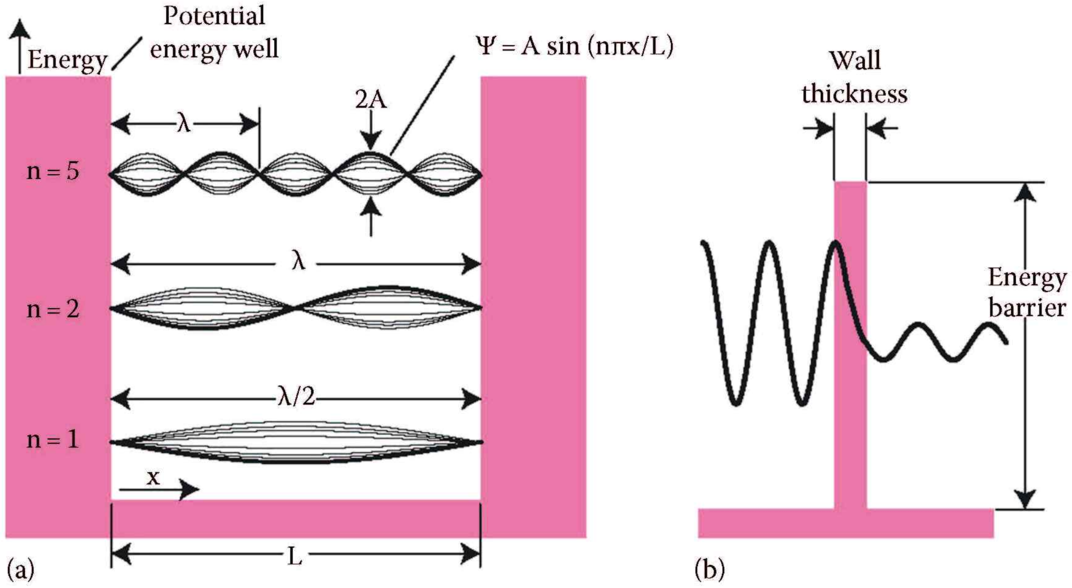


Figure 4.25 Illustration of electron (a) in infinite potential energy well (box) and (b) tunneling through an energy barrier (E_B). [Adapted from Rogers, B. et al., *Nanotechnology: Understanding Small Systems*, pp. 76, 217, CRC Press,

4.5.3 Energy Levels in Atoms

- The solutions to Schrödinger's wave equation provide the energy levels (or orbitals) that electrons can occupy in atoms.

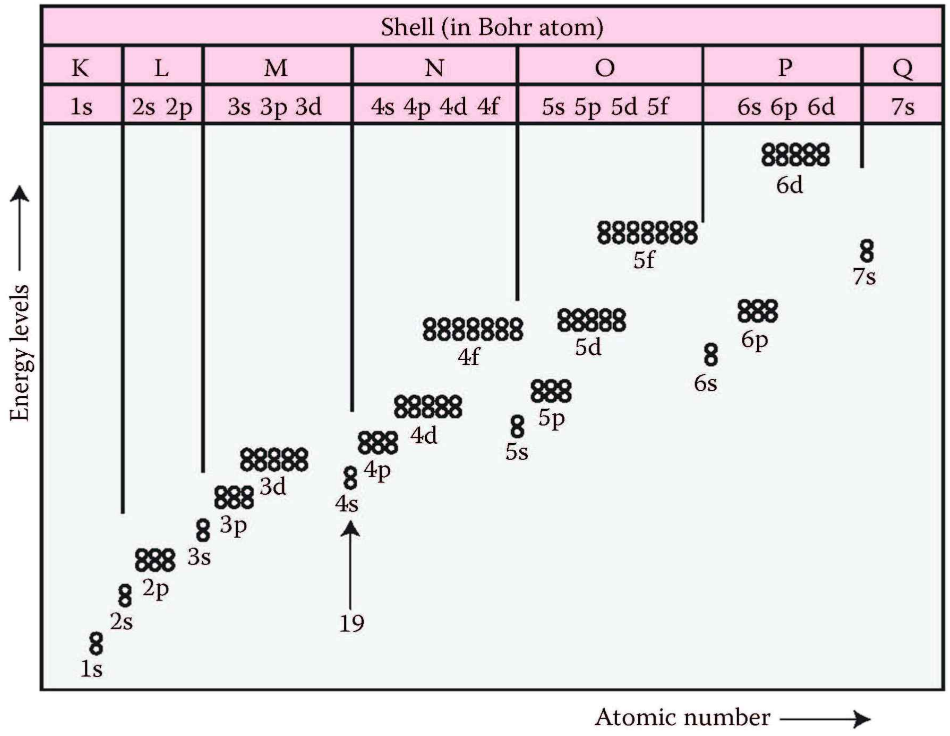


Figure 4.28 Energy level vs. atomic number for elements in the Periodic Table. Shells represent principal qu numbers (n = 1, 2, 3, …, 7). [Adapted from Rogers, B. et al., *Nanotechnology: Understanding Small Systems*

4.5.4 Structure of Molecules

- How are molecules put together?

1) Covalent bonding

- The combined probability of finding shared electrons between the nuclei is the product of the wave functions for the electrons on each nucleus.

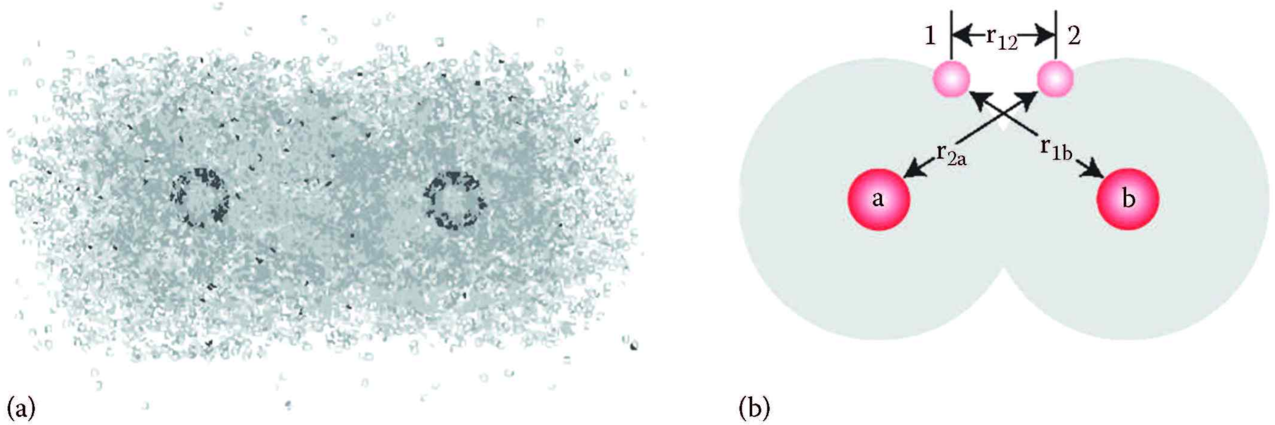


Figure 4.29 (a) Illustration of bonding between two hydrogen atoms [From Rogers, B. et al., *Nanotechnology: Understanding Small Systems*, CRC Press, Boca Raton, FL, p. 89, 2008.] and (b) the orbitals of electrons (1, 2) on nuclei (a, b). The arrows indicate the sharing of electrons 1, 2 with both nuclei, because the electrons are indistinguishable when they are between the atoms.

- The bonding in diamond: 4 carbon atoms are bonded together in tetrahedral geometry.
  The electrons are held tightly in covalent bonds, which accounts for the poor electrical conductivity.

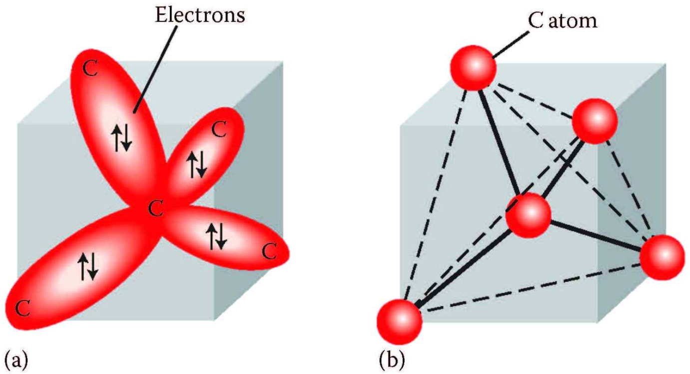


Figure 4.33 (a) Images showing the four bonds between the C atoms in diamond and tetrahedron between the C atoms. Arrows indicate overlapping (filled) orbitals. (b) The bonds and atoms are superimposed on a cube to show their arrangement. The dotted lines are faces of a tetrahedron with a C atom in the center of the tetrahedron and bonded to atoms on the corner of the cube.

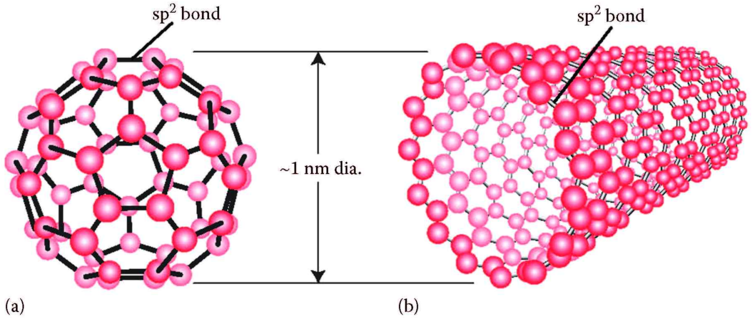


Figure 4.36 Illustration of two different carbon fullerene structures: (a) C60 buckyball and (b) single-walled carbon nanotube.

4.5.5 Band Structure of Solids

- Understanding metals (conductors), insulators, and semiconductors
- Energy bands are defined as the density of energy states (levels) that electrons occupy in a solid.

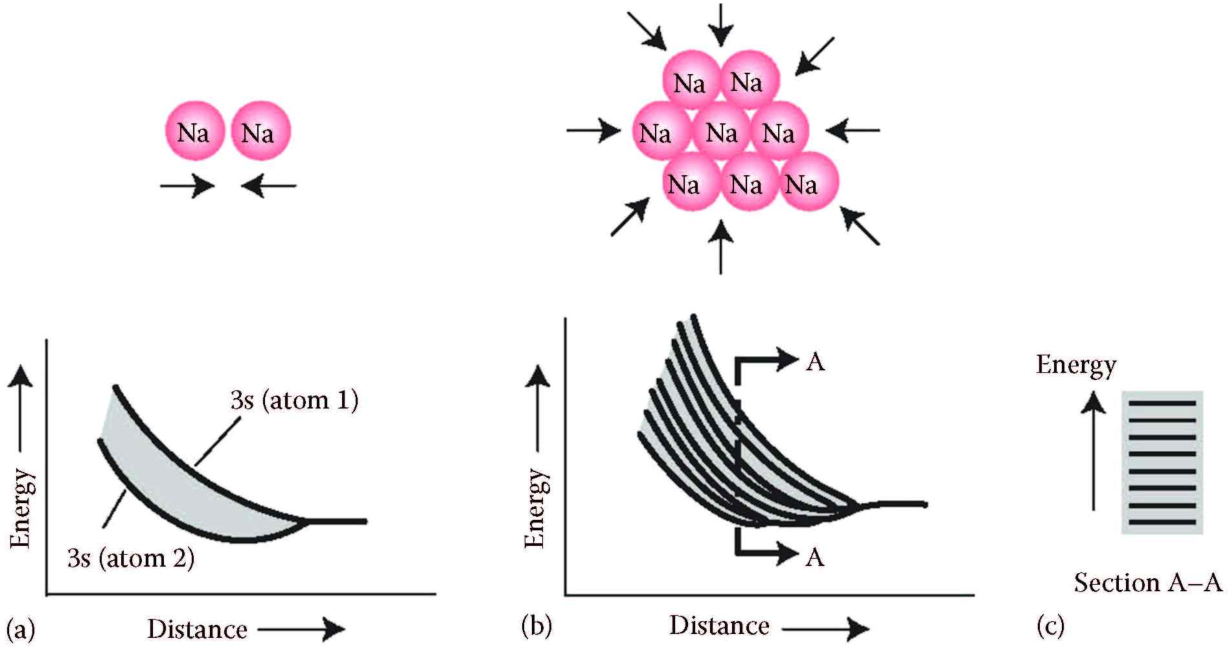


Figure 4.38 (a) Energy levels for 3s electrons as two Na atoms are brought together. (b) Energy levels for 3s electrons as eight Na atoms are brought together. (c) Cross section of energy levels. [Adapted from Rogers, B. et al.,

- The band gap is a forbidden zone that no electrons can occupy. In order to conduct, they must bridge the band gap and must be pumped from the "valence band" to the "conduction band".

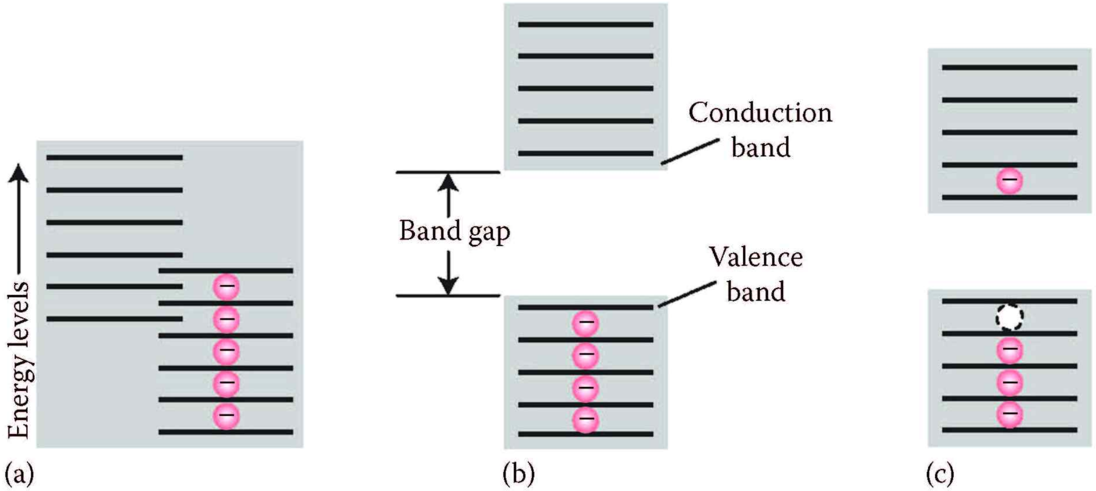


Figure 4.39 Illustration of energy bands for (a) metal (conductor), (b) insulator (nonconductor), and (c) semiconductor. [Adapted from Grove, A.S., *Physics and Technology of Semiconductor Devices*, p. 93, John Wiley & Sons, Inc., New

- In a semiconductor, there is a band gap but the gap is not as large as in insulators.
  The electrons can be pumped from the nonconducting valence band to the conduction band when enough energy or voltage is applied.
  When an electron moves from the valence band to the conduction band, it vacates an energy state and leaves behind a hole.

- Intrinsic and extrinsic (doped) semiconductors
  Extrinsic semiconductors are semiconductors that are alloyed with small amount of impurities (called dopants). These dopants increase the electric conductivity of silicon.
  N-type dopants add extra electrons to the Si structure and make it more electrically conductive through the reduction of the band gap.
  P-type dopants add small amount of holes that are electron vacancies or the absence of electrons.

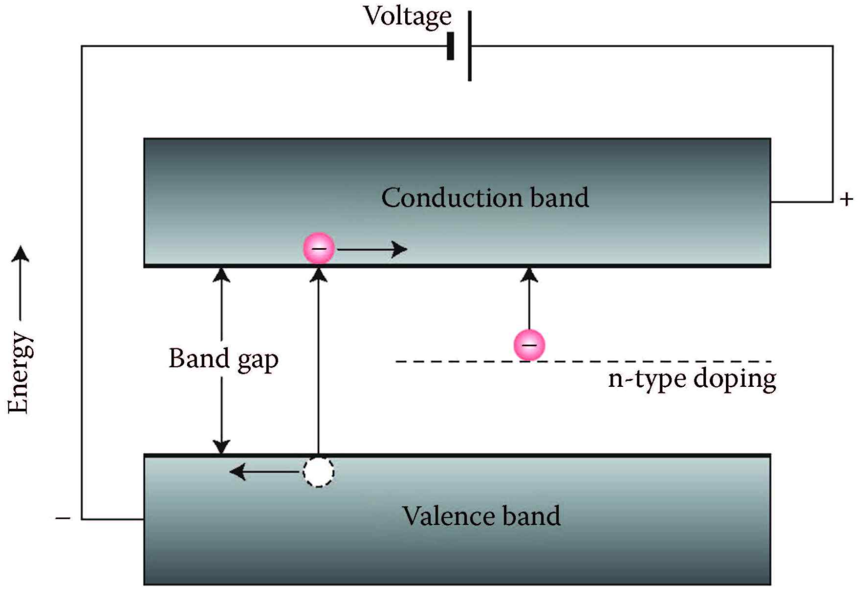


Figure 4.40 Energy band gaps of intrinsic and extrinsic semiconductors, where electrons are illustrated as red particles in the conduction band and extrinsic energy band. Holes are dotted circles.

4.5.6 Quantum Confinement

- Quantum confinement is a phenomenon that occurs when electrons in nanoparticles are squeezed into a narrow space.
- Electron confinement is just an extension of the “particle-in-a-potential well” model in quantum mechanics. As the size (L) of a nanoparticle decreases, its band gap increases ($1/L^2$ for the quantized energy levels in a potential well of length L).

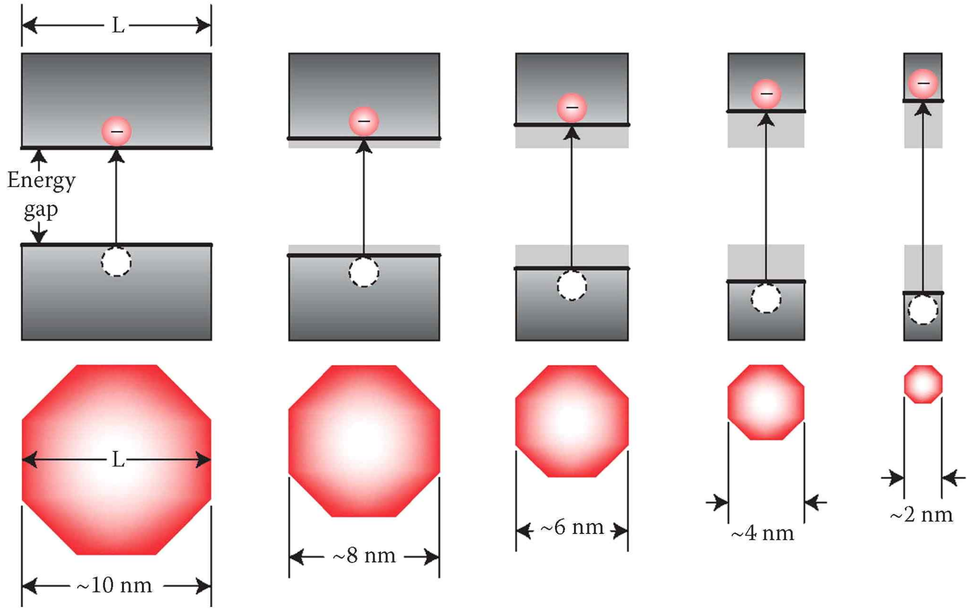
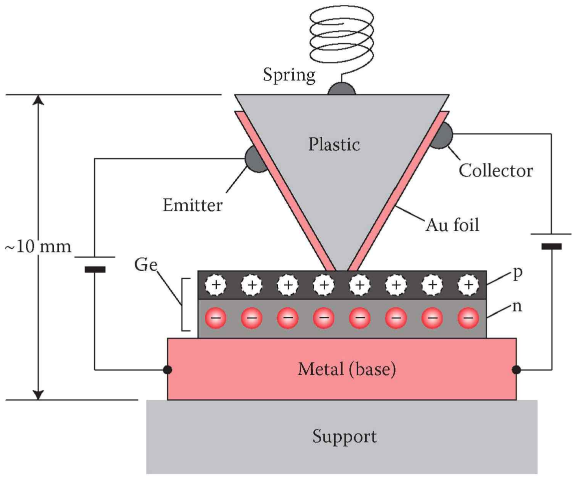


Figure 4.41 Schematic drawing on the size effect of Qdots on the apparent energy gap. Particle sizes are shown conceptually to decrease from 10 to 2 nm, which caused the energy gap to increase due to quantum confinement.

4.6 Benefits at the Bottom

4.6.1 Transistors Discovered

- The transistor was invented at Bell Lab. in 1947 by J. Bardeen, W. Brattain, and W. Shockley (1956 Nobel Prize); named by combining two words "TRANSfer resISTOR".
- Transistors are semiconductor devices that can act as either amplifiers or as on-off switches.
- The first transistor was made from a paper clip, metal contacts, gold foil, and a germanium (Ge) semiconductor (single crystal), and it was ~ 10mm in size.
  One gold contact was labeled as the "emitter", and the other was called the "collector".
  The conductive metal base was called the "base".



Schematic representation of the first transistor that was discovered by Bell Labs in 1947.

4.6.2 Light-Emitting Diodes (LEDs)

- Diodes are “pn junctions” consisting of n-type and p-type semiconductors that are joined together.

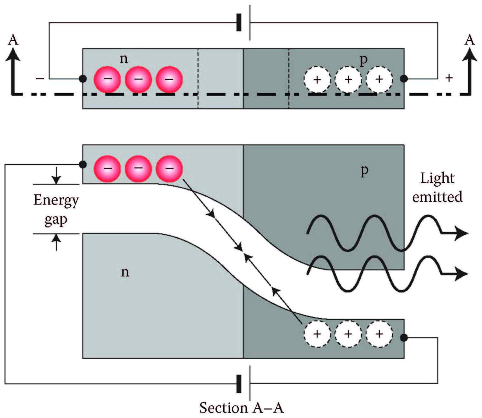


Figure 4.43 Drawing of LED with “p–n” junction formed by joining p-type and n-type semiconductors. A forward bias causes electrons (red particles) and holes (dotted circles) to recombine, which produces light. The device is sectioned to show the energy gap and electron-hole recombination.

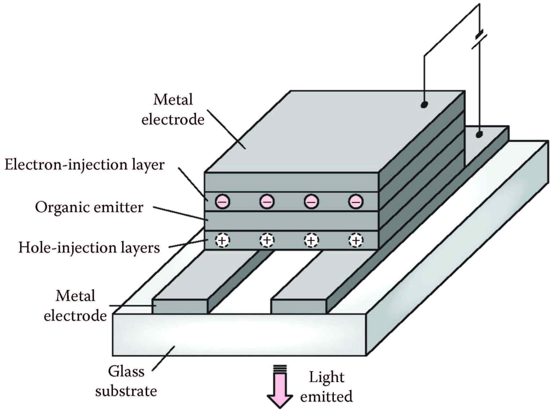


Figure 4.44 Schematic illustration of organic light emitting diode (OLED). Holes and electrons are injected into the organic emitter. When holes and electrons recombine, light is emitted. [Adapted from TC 201 Web Tutorial; https://

4.6.4 Nanotubes and Graphenes

- Nanotubes can be imagined as graphite layers that are rolled up into cylindrical shapes.
  The different rolled up orientations are called chilarity, which occurs in the form of three types of nanotubes – *armchair*, *zigzag*, and *chiral*.
- Graphene is a single layer of carbon atoms that has a honeycomb (hexagonal) structure.

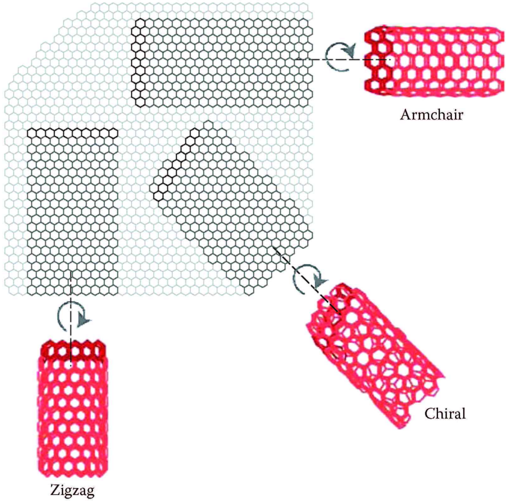


Figure 4.46 Different carbon nanotube structures (armchair, zigzag, and chiral) formed by rolling-up graphite sheets in different orientations. [Adapted from Rogers, B. et al., *Nanotechnology: Understanding Small Systems*, CRC

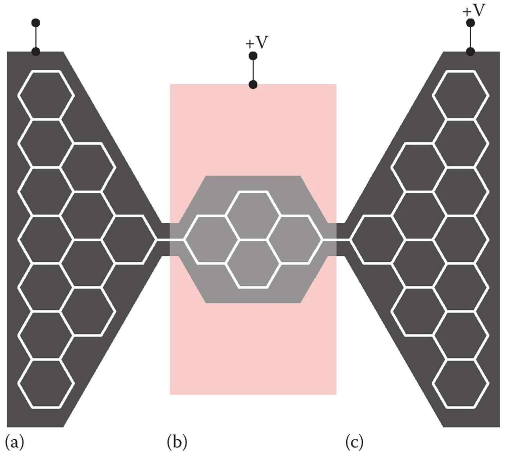


Illustration of graphene FET with (a) source, (b) gate, and (c) drain, where V = applied voltage.

[Homework/Reading Assignment]

1. Billinge, S. J. et. al., The problem with determining atomic structure, *Science*, 316, 561 (2007).
2. Westerbelt, R. M., Graphene nanoelectronics, *Science*, 320, 324 (2008).