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Nanotechnology: What, Why, and Why Now?

> *…the builder's final frontier…*
>
> Richard Smalley, Nobel Laurate in Chemistry, 1943–2005

1.1 What Is Nanotechnology?

Nanotechnology is the nexus of engineering, medicine, and science. It is not a discipline in the traditional sense but a broad spectrum of human endeavors unified by thinking, exploring, and creating at the size scale of things like molecules and viruses. This is the size scale where it is possible to achieve advances ranging from targeted therapies for breakthroughs in disease treatment to light weight, strong hierarchical materials for high speed, safe transportation. The prefix "nano" in the word "nanotechnology" comes from both Greek and Latin. In both languages it meant "dwarf," as it still does in modern Italian. The term "nanotechnology" is used in this text to describe the practice of engineering, medicine, and science in this world of things of the size of viruses and molecules – the nanoscale. This size range is defined here to be from a nanometer (10^{-9} m = nm) or a little smaller (down to tenths of a nanometer) to 100 nm or a little larger (up to several hundred nanometers). Figure 1.1 shows how this nanotechnology range fits in among the micrometer (10^{-6} m = μm), picometer (10^{-12} m = pm), and femtometer (10^{-15} m = fm) size ranges. It also includes a few examples from these size scales. The boundaries of the nanotechnology size range are taken in this text to be fuzzy, not sharp. Structures in the nanosize range are constructed by putting varying amounts of atoms or molecules or both together in new ways with new results. In the pico- and femto-scales, things are being done at the scale of an atom or its nucleus. Aside from radioisotopes and nuclear reactors, there is no corresponding picotechnology or femtotechnology. For a more complete overview of size scale terminologies, we have additionally included a broader, more encompassing size range in Figure 1.1, which is denoted as the "mesoscopic" scale. This scale term is sometimes used, principally in physics, to denote a wide range of sizes from that of an atom to micrometers (microns).

To get an idea of how many atoms we are working with in nanotechnology, we note that a typical solid has something of the order of 10^{22} atoms/cm^3. This means

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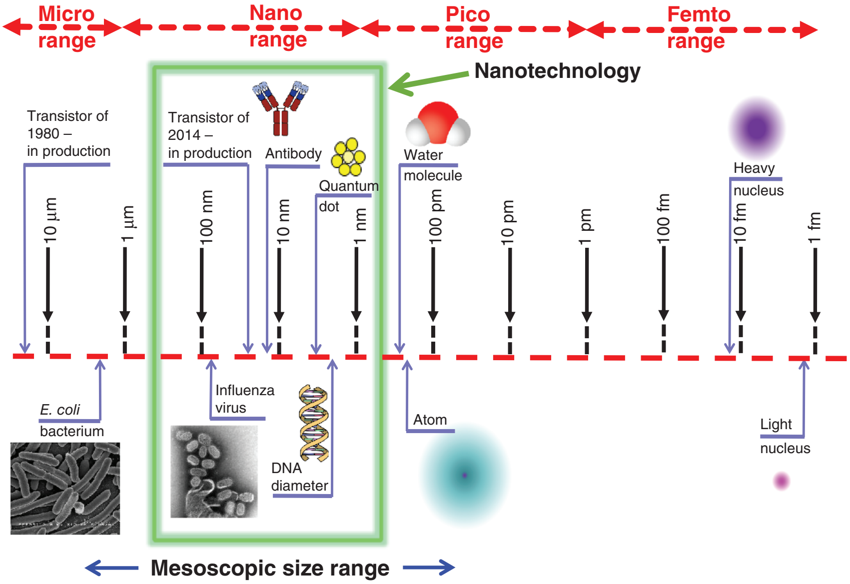

Figure 1.1 A schematic showing where nanotechnology lies among the micro-, nano-, pico-, and femtoranges. Some natural as well as man-made examples from these different size ranges are sketched (not to scale). Nanotechnology is formally defined as working with objects with at least one dimension in the 1–100 nm range. We will think of nanotechnology as having somewhat broader, diffuse boundaries as conveyed by the green box.

that a 100-nm-diameter nanoparticle contains $\approx 5 \times 10^6$ atoms, a 10 nm particle contains $\approx 5\times10^3$ atoms, and a 1 nm particle contains ≈ 5 atoms. The excitement of nanotechnology comes from the fact that its structures are so small and from the fact that phenomena dominating for these relatively minute assemblages of atoms can be very different from those dominating at the micrometer and larger scales. Nanoscience, nanoengineering, and nanobiomedicine strive to exploit the resulting opportunities available at the size scale of nanotechnology to create new manufacturing approaches, new materials, and new structures for the betterment of society.

Because of this excitement and intense activity at the size range of objects such as viruses and molecules and because of its broad applicability, nanotechnology has received a great deal of public attention and "hype." Some may say it has been overhyped. What seems closest to the actual situation is that the timeline over which nanotechnology can deliver society-changing results has been underestimated. The application of nanotechnology has turned out to be often much easier in science than in engineering or medicine, both of which can entail dealing with economic and societal issues. A common failure has been to assume that, once a new basic nanomaterial or device has been created, or that a fundamental phenomenon has been observed, the step of employing it in an engineering or medical field is straightforward. In fact, the opposite is usually true. Developing something of societal impact – the making of a nanotechnology science advance into something practical, environmentally compatible, economically viable, and commercially manufacturable – is usually the more difficult task.

Nanotechnology has already contributed to addressing crucial issues such as defeating cancer, providing clean energy, and protecting the environment. It has already produced incredible advances in fields such as electronics, optoelectronics, and biomedical imaging. While it has not yet produced materials that will withstand the perils of any car accident, it has produced miniature sensors, computational circuits, lasers, and so on that make possible accident-avoidance cars and trucks and even fully self-driven vehicles. The needs of the twenty-first century are being addressed by nanotechnology but many challenges remain. We still need more contributions from nanotechnology to attain adequate water and energy resources for the future, reduction of scarce-materials usage, reduction in deleterious human impact on the planet, and enhanced control of diseases.

1.2 Why Is Nanotechnology So Unique?

The excitement and possibilities of nanotechnology become apparent when one simply asks the question "what are the unique features of this size range?" It turns out that, by our count, there are 10 answers. The first unique feature of the nanotechnology scale is the obvious one: nanotechnology sizes are very small. They are so small that they are in the same size realm of very basic biological and physical objects. For example, the sizes of pores in cell walls, of viruses, and of the diameter of DNA are all in the size realm of nanotechnology. The second unique feature is that the surface to volume ratio (which of course goes as $1/r$ for particles of radius r) can clearly be very large. This means the surface properties and surface forces can be very important relative to their bulk counterparts. For example, gravity, a bulk force, can be negligible with respect to surface interactions for particles in the nanotechnology range. In one of his famous three 1905 papers, Einstein realized that gravity was unimportant for nanoparticles in solution (then referred to as colloidal particles). He realized that in undergoing Brownian motion, such very small particles were only subject to surface forces. As long as they did not agglomerate due to surface bonding as they bounced around in their collisions with other particles, atoms, and molecules, they could stay in solution forever [1].

The increasing surface to volume importance with decreasing nanoparticle size is the basis of the third feature: that the atoms or molecules on the surface of a nanoparticle become increasingly important, compared to those in the interior, as Figure 1.2 suggests. Since these atoms "see" a different environment than those in the interior (bulk) and the number affected varies with the radius, the physical and chemical properties of a particle can change with radius. Experimental evidence emphasizing this point is offered in Figure 1.3, which shows data for the melting temperature of Au versus nanoparticle size [2].

A fourth unique feature of the nanotechnology size range is that remarkable forms of chemical bonding can exist for nanoscale structures. A very well-known demonstration of this phenomenon can be found in single wall carbon nanotube

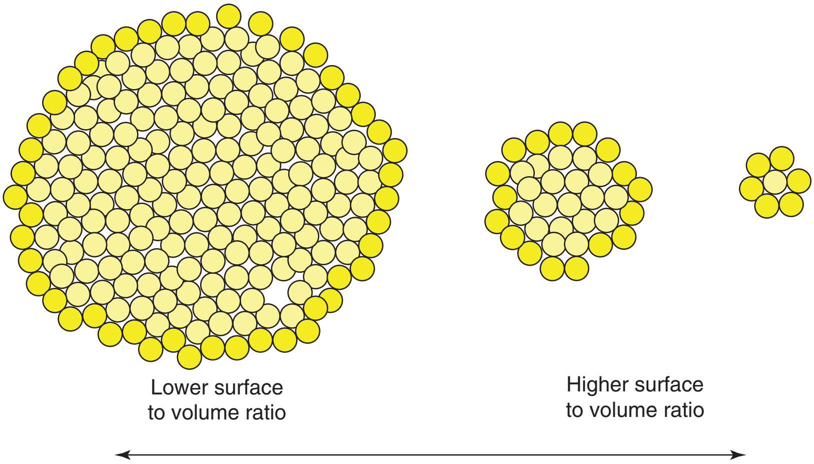

Figure 1.2 A pictorial representation of the increasing role of surfaces as particle size diminishes.

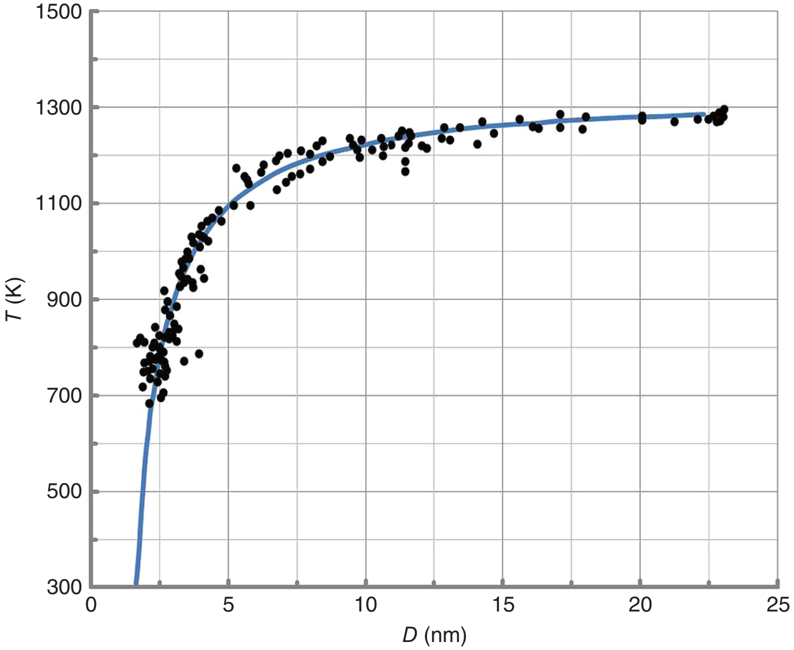

Figure 1.3 The melting temperature of Au as a function of particle diameter. The curve has been added to aid the eye. (© 1976 American Physical Society. Reprinted figure with permission from [2].)

(SWCNT), depicted in Figure 1.4. This figure shows the single sheet of atoms of the SWCNT has features of the hexagonal bonding of carbon in graphene and graphite (see Section 3.2.4.1). However, unlike graphene or graphite, this bonding present in the SWCNT is contorted. The contortion can have variable amounts of twisting depending on the process that produces the SWCNT. In any case,

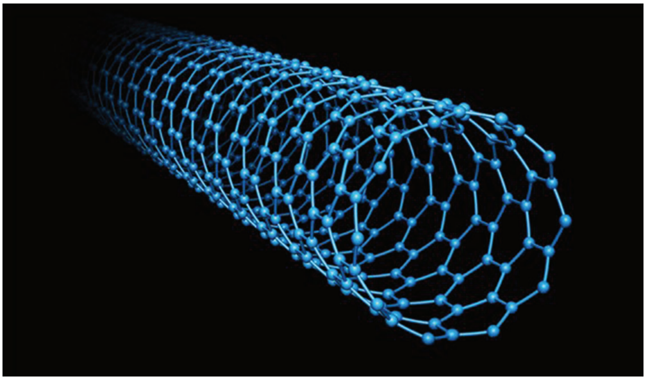

Figure 1.4 The single wall carbon nanotube (SWCNT). Carbon atoms are represented by the spheres. (Reprinted with permission from http://www.tinymatter.com/.)

this single atom layer thick sheet of the SWCNT is clearly stressed. Amazingly, even with this twisting, these ~1-nm-diameter tubes are six times stronger than steel [3].

The fifth unique feature found in the nanotechnology realm is the phenomenon of self-assembly. Self-assembly is found in many forms in nature. At the nanoscale, it can be exploited and controlled; that is, we have learned to be able to create conditions at the nanoscale where particles, atoms, or molecules can self-assemble themselves into predetermined new materials and structures. Figure 1.5 gives an example. Here, it can be seen that nanocrystal particles have self-assembled into a new honeycomb two-dimensional (2D) crystalline material with atomic as well as nanoparticle order [4]. Such new materials can have properties that are different from the material comprising the constituent nanoparticles [5].

The sixth and seventh unique features that are available to be exploited at the nanoscale have their basis in quantum physics, which can dominate in this size range. Because of this, the concepts of quantization, quasi-particles, and wave–particle duality are able to contribute to everyday working ideas in nanotechnology. We first consider the sixth feature: quantization and its dependence on size. Figure 1.6 schematically captures the quantization of energy and its dependence on size as it may be easily seen experimentally in nanoscale semiconductor materials called quantum dots (QDs). This class of nanoparticles, typically 1–10 nm in size, have good absorption of light and they have forbidden energies (band gaps) E_g that depend on the particle size. The QDs in this figure are all made of the same semiconductor and are all subject to the same external monochromatic light with a wavelength λ and a photon energy greater than that all the E_g values. The figure shows what happens experimentally when this monochromatic light of wavelength λ impinges onto these five nanoparticles of different sizes. As seen, the monochromatic light is absorbed by all the QDs since the energy of its photons is larger than any of the E_g values but 5 wavelengths of light leave with λ's that depend on particle size. Through Planck's relation $E = hc/\lambda$ where h is Planck's constant and c is the speed of light [6], it is clear that

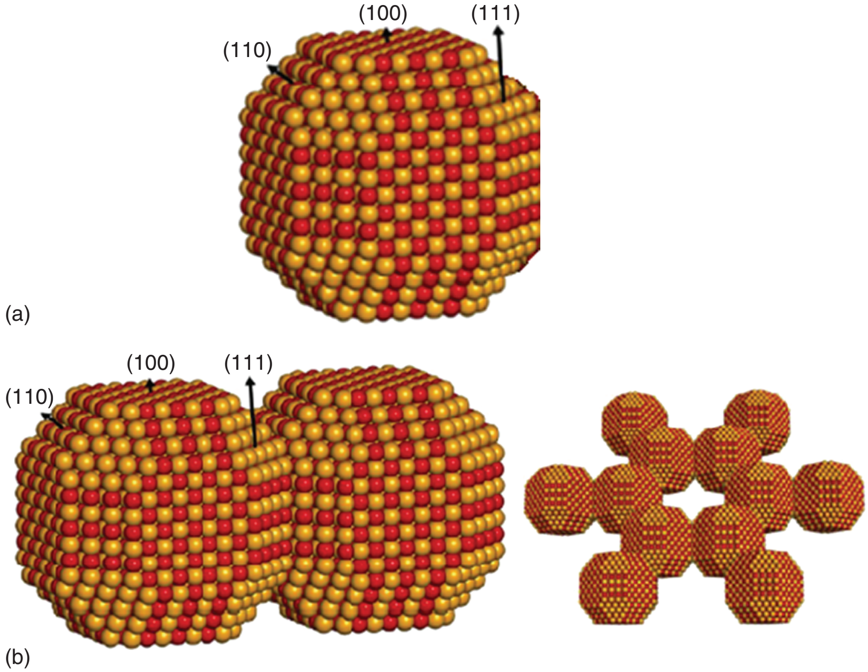

Figure 1.5 A representation of the formation of a new material by self-assembly involving (a) nanocrystal particles which have (b) self-assembled at the same crystallographic plane of each particle. In this example, two nanoparticles (nanocrystals) are self-assembling by attaching at {100} planes. The right shows 12 nanoparticles assembled into a lattice bonded at {100} planes. (The {100} notation is an example of a plane-naming scheme called Miller indices. There are Miller indices to denote directions, as well as crystallographic planes in a crystal. Miller indices are discussed in a number of standard materials texts.) (© 2013 American Chemical Society. Reprinted and adapted with permission from [4].)

photons of one single energy are arriving but photons with 5 different energies are leaving. Each QD only emits photons with its unique energy E_g and this energy depends on its size.

Let us digress here to discuss Figure 1.6 in more depth and to stress some points. We do this since quantization and its dependence on size at the nanoscale are so important. The absorption of the incoming light and its subsequent emission (called fluorescence) at five different wavelengths are due to electrons that are excited by the incoming light and then relax by losing different amounts of energy in the five samples as they undergo transitions from excited levels through heat loss to the lowest excited level (called the conduction band edge), and then finally through photon emission to their highest ground state energy (called the valence band edge). As seen from the light colors (i.e., wavelengths) in the figure, the wavelength or equivalently energy difference given by the quantity (lowest excited energy – highest ground state energy) depends on nanoparticle diameter. This energy difference is called the semiconductor forbidden energy gap or just the band gap E_g, as noted. Looking at the figure, we see that the energy E_g can only take on a specific value for each QD (it is quantized) and this value depends on the QD size.

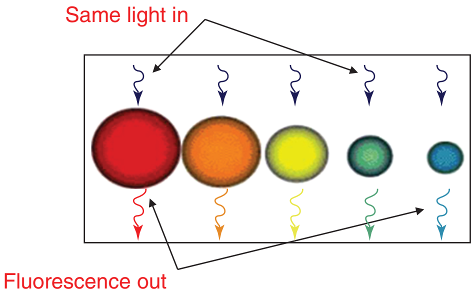

Figure 1.6 Fluorescence response to a monochromatic light source as a function of the relative size of semiconductor nanocrystals (quantum dots). The fluorescence response is seen to depend on the nanoparticle size. (From Invitrogen Corporation (2009), with permission. https://www.thermofisher.com/us/en/home/brands/molecular-probes/key-molecular-probes-products/qdot/technology-overview.html#structure?icid=fr-qdot-3 (6 June 2017).)

Digressing a bit more, we can develop a simple mathematical model that allows us to understand why energies depend, at the nanoscale, on size by using the mathematics of the famous "particle in an infinitely deep box" construct [6]. In our use of this model, the particle is an electron and we treat a QD as a box with sides of length L and with infinitely high potential energy "walls" trapping the electron. Of course, a nanoparticle such as that seen in Figure 1.2 is not a box but we are just attempting to get some insight into how the nanoparticle size affects the energies allowed to the electrons in a QD. Using the results of the particle in an infinitely deep box problem shows that the energies allowed to an electron in any one of our five boxes are quantized to certain values and these obey [6]

$$E = \frac{h^2}{8m_\mathrm{e} L^2}\left[n_x^2 + n_y^2 + n_z^2\right] \tag{1.1}$$

where L characterizes the dimensions of the 3D box under consideration. In this equation, m_e is the mass of an electron and n's are the quantum numbers and can independently take on the values $1, 2, 3, \ldots$. There are three quantum numbers because, when a particle is confined to a 3D situation, there is a spatial quantum number for each dimension of confinement [6]. Since the energy gap E_g is the difference between two adjacent, allowed energy levels in a QD, Eq. (1.1) indicates that E_g should vary something like $1/L^2$. This cannot be quite correct because, as we have said, a QD is not a box and does not have an infinitely deep potential energy well. However, the insight that emerges is that an electron (i) gets excited across a QD band gap by the incoming monochromatic light in Figure 1.6, then (ii) thermalizes to the lowest excited state energy (the conduction band edge) by losing energy as heat,[1] and finally (iii) emits light (a photon) to relax back across the energy band gap to the highest ground state. And the energy difference between the lowest excited state and the highest ground state of the QD (the emitted photon energy) scales something like $1/L^2$. This is seen in the interconnection between the wavelength of light, and the color perceived by the human eye seen

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[1] Band gap, conduction band, valence band, thermalization, and fluorescence are all discussed in Chapter 5.

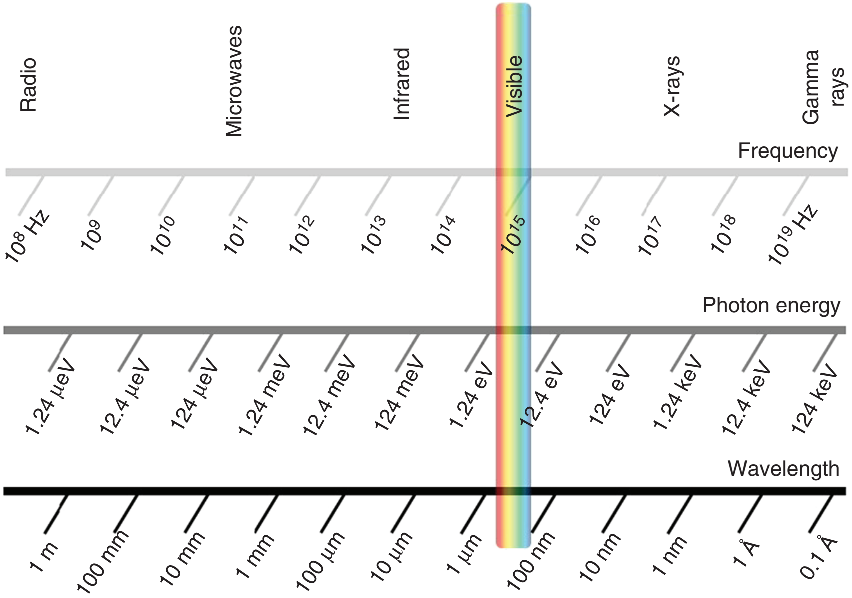

Figure 1.7 The relationship between wavelength range designation, frequency, photon energy, and wavelength for the electromagnetic spectrum. The section in color is the range which the human eye can detect.

in Figure 1.7. This simple example of Figure 1.6 demonstrates energy is quantized to only certain allowed values and these vary with size, at least at the nanoscale. The nanoscale is special because all of this becomes imperceptible as L gets large, as seen from Eq. (1.1). This discussion also underscores that we need to think of the interaction between light and materials in terms of an electromagnetic field quasi-particle called the photon. Soon we will get so comfortable with the photon and other quasi-particles that we will simply accept their role in nature. In Chapter 5 we will do a more careful job at looking at the states available in solids.

At the nanoscale there is also a clear emergence of what we term feature seven: the wave–particle duality concept of quantum mechanics (see Section 2.2.2). Figure 1.8 demonstrates an aspect of this wave–particle duality feature which can be prominent at the nanoscale by presenting experimental probability density data giving the location of electrons trapped in a "corral" of atoms sitting on a surface. As we will discuss in Chapter 2, this quantum mechanical probability density is given mathematically by $\Psi(\vec{r},t)\Psi^*(\vec{r},t)$, where $\Psi(\vec{r},t)$ is the wavefunction resulting from solving the Schrodinger wave equation of quantum mechanics. The quantity $\Psi^*(\vec{r},t)$ is the complex conjugate of $\Psi(\vec{r},t)$ [6]. To be more specific about this figure, we note that it shows atoms sitting on top of a surface (whose own atoms are also discernable). These atoms on top of the surface have been dragged into a "corral" configuration with a nanoscale probe. Valence electrons from these dragged atoms have gone into the corral and their resulting experimental position distribution $\Psi(\vec{r},t)\Psi^*(\vec{r},t)$ is clearly seen; actually, it is not a function of time in this case so we should write

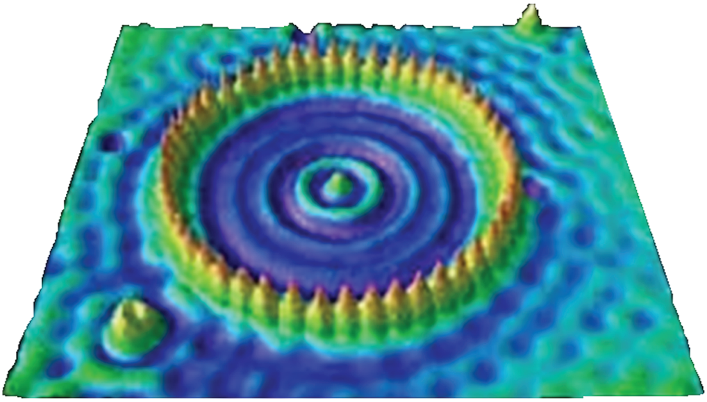

Figure 1.8 Atoms arranged on a surface to form a corral confining their valence electrons. The probability density distribution image has been captured by scanning tunneling microscopy. (Reprinted with permission from AAAS [7].)

$\Psi(\vec{r})\Psi^*(\vec{r})$. Interestingly, this probability wave function $\Psi(\vec{r})\Psi^*(\vec{r})$ in this situation looks like a stationary wave pattern on a drumhead. The $\Psi(\vec{r})\Psi^*(\vec{r})$ we see in Figure 1.8 has been experimentally imaged using what is termed a scanning tunneling microscope (STM) [7], a tool discussed in depth in Section 7.3.1.5. The image is created by drawing (tunneling) electrons out of their predicted positions $\Psi(\vec{r})\Psi^*(\vec{r})$ using a scanning nanoscale probe biased positively with respect to the surface, keeping track of the current at each point, and turning that electrical current into an image of $\Psi(\vec{r})\Psi^*(\vec{r})$. The more current at a point, the larger is the $\Psi(\vec{r})\Psi^*(\vec{r})$ at that point. The electrons move from the corral to the probe tip because their wave function leaks from one to the other by this "tunneling," a quantum mechanical process discussed in Section 2.2.4.1. Figure 1.8 may be summarized by noting that we are actually "seeing" (through a computer construct generated from electron tunneling current) the quantum mechanical wave probability distribution $\Psi(\vec{r})\Psi^*(\vec{r})$ of the corralled electrons.

Some very interesting relativistic/quantum mechanical phenomena can also be found in the nanotechnology size range. We classify these as the eighth unique feature of the nanoscale. These nanotechnology relativistic/quantum mechanical features result in materials with mass-less electrons and materials with electrons whose momentum and quantum mechanical spin are interlocked. As a result, relativity can have an amazing influence on transport properties at the nanoscale. These features are discussed in more depth in Section 5.2.2.3.

Because things are so small, nanotechnology materials can also display another unique aspect, termed fluctuations, which is the ninth feature in our listing of remarkable aspects of the nano-scale. This feature encompasses both thermal and quantum fluctuation effects. Their origin lies in the very small number of atoms or particles that may be involved in nanostructures and the resulting quantum and thermal fluctuations that may be observable. These phenomena are discussed in Sections 2.2.4.3 and 2.2.5.2.

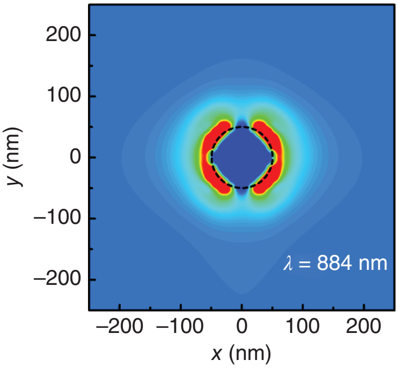

Figure 1.9 Computer simulation giving the light intensity around a Ag nanoparticle produced by a plane wave (wavelength 884 nm) impinging from large y onto the particle. Surface plasmon excitation at the Ag nanoparticle periphery is seen, as is the near-field region.

The final unique attribute of the nanotechnology size range which we have on our list is feature 10: the unique material–light (electromagnetic radiation) interactions that can occur at the nanoscale. These can involve both quantum phenomena as well wave (physical optics) effects. Figure 1.9 shows such a situation. Here, what is termed the plasmonic mode of a metal nanoparticle has been excited by the electric field of an incoming light wave. This mode is a cooperative excitation of the essentially free, valence electrons of a metal nanoparticle. In this mode, the electrons are following the electric field by sloshing back and forth, in phase, throughout the particle. For this in-phase movement to be possible, the wavelength λ of the incoming light must be large compared to the diameter $2r$ of the nanoparticle; that is, the electrons in the nanoparticle must “feel”, at any time t, essentially the same electric field ξ everywhere in the particle. For a metal nanoparticle of diameter 10 nm, this criterion is easily met by infrared (IR), visible and near (to blue) ultra-violet (UV) light, as seen from Figure 1.7. This plasmon excitation (the electrons sloshing in phase), as a quantum of this oscillating electron motion is called, can relax resulting in the reradiation of photons from the nanoparticle. In addition, energy can also be lost due to collisions of these oscillating valence electrons within the particle. The electric field distribution caused by the plasmon excitations of the metal nanoparticle has a radiating far-field component corresponding to the emitted photons and a strong near-field component (the electric field around the nanoparticle). This high field is seen to fall off in Figure 1.9 with a characteristic length of the order of the nanoparticle size.

To summarize, the nanoscale offers 10 unique features. These are what make nanotechnology so interesting. They offer new opportunities for new products, new materials, new methods, and new structures. To summarize the 10 are the following:

1. Nanotechnology sizes are in the realm of very basic biological and physical objects.
2. The surface to volume ratio of nanostructures can be very large causing surface phenomena to dominate over bulk phenomena.
3. The physical and chemical properties of a nanoparticle can change with size.
4. Unique forms of chemical bonding can exist for nanoscale structures.
5. Self-assembly can be initiated and controlled at the nanoscale.

6. The quantized nature of energy and fields (quasi-particles) can become important for nanotechnology materials and structures.
7. Wave–particle duality can play an obvious role at the size range of nanotechnology.
8. Relativistic/quantum mechanical effects can play a role in some nanomaterials.
9. Thermal and quantum fluctuation effects can be important.
10. Material–electromagnetic radiation interactions can involve quantum and physical optics phenomena at the size range of nanotechnology.

1.3 Where Did Nanotechnology Come From?

Nanotechnology did not suddenly appear; it actually has a long history. Humans have been involved with man-made nano-particles since dealing with soot in the first fires [8]. An early example of where nanotechnology was purposefully used appears in Greek–Roman hair-dyes. Of course, the Greeks and Romans could not see and did not know about nanoparticles but they knew that their hair dye formula worked very well – for some reason. Today, we know it worked due to the nanoparticles in the dye and the formation of $\sim$5 nm nanocrystals deep inside strands of hair giving rise to color change [9]. The Romans created more technology based on the nanoscale with their development of glass, apparently containing unwittingly tiny amounts of colloidal gold and silver. An outstanding example of this Roman nanotechnology is the so-called Lycurgus Cup, which dates back to over 1600 years ago, and is today located in the British Museum. The Cup is an opaque green when white light impinges on it. However, when white light is allowed to shine through the Cup, it turns to a glowing translucent red. Today, this response is believed to be due to plasmonic effects arising from the metal nanoparticles [10, 11]. We have to assume that the Romans only knew that they had a winning formula for making a very interesting piece of art.

During the Middle Ages, Arab craftsmen made steel swords of legendary strength. Investigation has shown that the material of these swords contains carbon nanotubes and nanowires. This technology, dating back to about 1000 years ago, is the oldest known purposeful use of carbon nanotubes and nanowires. We can only imagine someone unknowingly stumbling onto a procedure that yielded this high-quality nanostructured material and wisely hiding the recipe [12]. During the late Middle Ages, European craftsmen reintroduced the use of metal nanoparticles in glass and ceramics and by the Renaissance, Italian artisans were using metal nanoparticle plasmonic effects to give color to ceramics [13].

While people were seemingly unwittingly using nanotechnology in these examples, we can single out the work of the English scientist Michael Faraday in the mid-nineteenth century as the beginning of a true awareness and understanding of the nanoworld. Faraday realized that colloidal solutions made by reducing a gold-bearing salt (e.g., $NaAuCl_4$) contained very tiny particles of Au in the solution and he noted that “known phenomena appeared to indicate that a mere variation in the size of its particles gave rise to a variety of resultant colors" [14,15]. As mentioned earlier, some 50 years later Einstein explained why these particles stayed in solution [1]. Also, about 50 years after Faraday's work, Austrian-Hungarian chemist Richard Zsigmondy made a detailed study of gold colloid solutions and other nanomaterials with sizes down to 10 nm and below and published a book on his work in 1914. He used a microscope that employed the dark field method of imaging particles that were much smaller in size than the wavelength of the light employed. Zsigmondy, a Noble laureate for his work with colloids, coined the term nanometer for 10^{-9} m and used the terminology in characterizing particle sizes in what we now call the nanoscale [16].

In 1931, the German team of physicist Ernst Ruska and electrical engineer Max Knoll successfully made the first demonstration of an imaging technique, which today is known as transmission electron microscopy (TEM). Within two years the resolution of this tool was surpassing that available from optical microscopes of the day [17]. This was because the wavelength of the quantum mechanical wave function Ψ of an electron is much smaller than the wavelength of light. Further progress in nanotechnology occurred in the same decade (specifically in 1932) when the Americans Irving Langmuir and Katharine Blodgett developed a technique for controllably producing films a monolayer (single molecule) in thickness [18]. In 1959, American physicist Richard Feynman gave his now often cited "There's plenty of Room at the Bottom" address [19] in which he posited that science and technology had progressed to the point where we could and should manipulate matter at what today we call the nanoscale. In 1974, Japanese processing engineer Norio Taniguchi introduced the term nanotechnology in his work on precision control of semiconductor device fabrication [20].

Continuing this short history of nanotechnology, we come to the decade of the 1980s which we will consider the beginning of the modern era. In 1981, German physicist Gerd Binnig and Swiss physicist Heinrich Rohrer introduced the STM [21], the first scanning probe tool capable of atomic resolution. As we will see in Chapter 6, the STM has evolved today into a myriad of scanning probe tools for atomic manipulations, imaging, and physical property measurements. In this decade the American chemists R. Smalley and R. Curl along with the English chemist H. Kroto discovered Buckey balls. These have the famous nanoscale carbon 60 "soccer ball" structure [22]. This was the first of the many nanotechnology materials that are the topics of discussion in Chapter 5.

1.4 Why Has Nanotechnology Burst Forth Now?

After a long period of a few applications here and there nanotechnology has emerged, especially in the last several decades, as a very vibrant, productive area of endeavor permeating science, engineering, and medicine. Why has so much occurred so recently? Two factors are involved: one is that we have learned to work comfortably at the nanoscale and the second is that we have learned to be able to "see" what we are doing at the nanoscale. Microelectronics, which Figure 1.1 shows should really be called nanoelectronics today since its transistors are now in nanoscale, has been a huge part of establishing this comfort. It has driven the development of precision nanoscale processing and characterization. As a result, in the twenty-first century, nanoscale processing has become so efficient that we manufacture more transistors in a year than we grow grains of rice [23]. And with the characterization techniques available, we can "see" all sorts of nanoscale structures that we or nature makes – from Buckey balls and QDs to viruses and DNA. Nanotechnology is just now beginning to demonstrate its potential to create many new materials and devices with a vast range of applications covering diverse areas such as medicine, electronics, biomaterials, energy production, and consumer products. As with any new technology, probably starting with the discovery of fire, nanotechnology is raising concerns about its health and environmental impact as well as concerns about who in society benefits. This is as it should be.