CHAPTER 1

Size Matters

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1.1 THE FUNDAMENTAL IMPORTANCE OF SIZE

The aim of this chapter is to instill an intuitive feel for the smallness of the structures that are used in nanotechnology and what is special about the size range involved. As we will see, the importance of the nanoscale is wrapped up with fundamental questions about the nature of matter and space that were first pondered by the ancient Greeks. Three thousand years ago, they led the philosophers Leucippus and Democritus to propose the concept of the atom. These ideas will come around full circle at the end of the book when we will see that modern answers (or at least partial answers—the issue is still hot) are very much wrapped up in nanotechnology.

First of all, let us remind ourselves how small nanostructures really are. This is a useful exercise even for professionals working in the field. The standard unit of length in the metric system is the meter, originally calibrated from a platinum–iridium alloy bar kept in Paris but since 1983 has been defined as the distance that light travels in 1/299,792,458 seconds. For convenience, so that we are not constantly writing very small or very large numbers, the metric system introduces a new prefix every time we multiply or divide the standard units by 1000. Thus a thousandth of a meter is a *milli*-meter or mm (from the Roman word *mille* meaning 1000); a thousandth of a millimeter (or a millionth of a meter) is a *micro*-meter or μm (from the Greek word *mikros* meaning small). Similarly, a thousandth of a micrometer (or a billionth of a meter) is a *nano*meter or nm (from the Greek word *nanos* meaning dwarf). As shown in Fig. 0.1 ("the nanoworld"), we will be dealing in building blocks that vary from 100 nm across down to atoms, which are 0.1 to 0.4 nm across.

Nowadays, instruments can directly image nanostructures; for example, Fig. 1.1 shows a scanning tunneling microscope (STM—see Chapter 4, Section 4.4.1) image of a few manganese nanoparticles with a diameter of about 3 nm

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Introduction to Nanoscience and Nanotechnology, by Chris Binns
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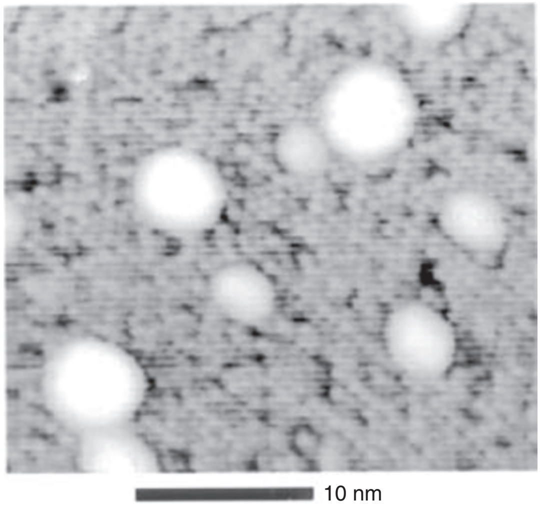

Fig. 1.1 Manganese nanoparticles on bucky balls. STM image (see Chapter 4, Section 4.4.1) of a few manganese nanoparticles with a diameter of about 3 nm (i.e. each one contains a few hundred manganese atoms) deposited onto a bed of carbon-60 nanoparticles with a diameter of 0.7 nm on a silicon surface. Reproduced with the permission of the American Institute of Physics from M. D. Upward et al. [1].

deposited onto a bed of carbon-60 molecules (“bucky balls”—see Chapter 3) with a diameter of 0.7 nm on silicon. It thus displays two different nanoparticles of interest in the same image. This could just as easily be a picture of snowballs on a bed of marbles, and it is easy to lose sight of the difference in scale between our world and that of the nanoparticles. To get some idea of the scale, take a sharp pencil and gently tap it onto a piece of paper with just enough force to get a mark that is barely visible. This will typically be about 100 μm or 100,000 nm across. If the frame in Fig. 1.1 were this large, it would contain about 100,000,000 of the Mn nanoparticles and 20,000,000,000 of the carbon-60 nanoparticles, which is about three times the population of the planet.

In fact, distance scales used in science go to much smaller than nanometers and much larger than meters, but the title of this book suggests that there is something special about the nanoeter scale—so what is it? The answer to this lies in philosophical questions that were originally posed regarding the fundamental nature of matter and space by Democritus and his contemporaries that still resonate today. Democritus (Fig. 1.2) was born in Abdera, Northern Greece in about 460 B.C. to a wealthy noble family, and he spent his considerable inheritance (millions of dollars in today’s currency) traveling to every corner of the globe learning everything he could. Known as the laughing philosopher, he lived to over 100 years old, so it appears to have been a good life. He wrote more than 75 books about almost everything from magnets to spiders and their webs. Only fragments of his work survived, with most of his books being destroyed in the

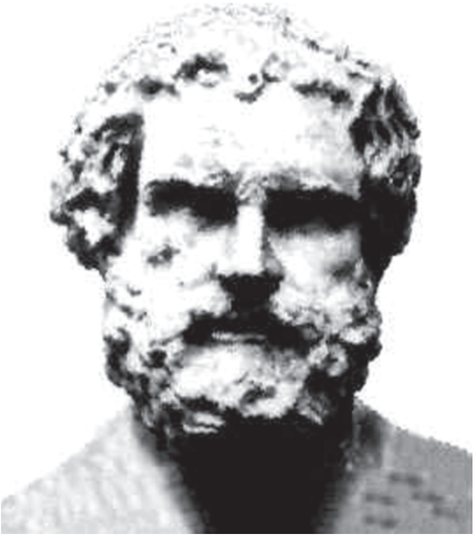

Fig. 1.2 Democritus. Marble bust of Democritus, Victoria and Albert Museum, London. Reproduced with permission from Carlos Parada, Greek Mythology Link: (http://homepage.mac.com/cparada/GML).

third and fifth centuries. His lasting impact on modern science was to propose, with his teacher Leucippus, the concept of the atom.

All our experience in the macroscopic world suggests that matter is continuous; and thus with nothing but our eyes for sensors, the original suggestion that matter is made from continuous basic elements such as earth, fire, air, and water seems reasonable. This, however, leads to a paradox because if matter were a continuum, it could be cut into smaller and smaller pieces without end. If one were able to keep cutting a piece of matter in two, each of those pieces into two, and so on ad infinitum, one could, at least in principle, cut it out of existence into pieces of nothing that could not be reassembled. This led Leucippus and Democritus to propose that there must be a smallest indivisible piece of substance, the *a-tomon* (i.e., uncuttable), from which the modern word *atom* is derived. They suggested that the different substances in the world were composed of atoms of different shapes and sizes, which is not an unrecognisable description of modern chemistry. Once you propose atoms, however, you automatically require a “void” in which they move; and the void is a concept that also produces dilemmas, which were the subject of much debate three thousand years ago. For example, is the void a “something” or a “nothing” and is it a continuum or does it also have a smallest uncuttable piece? Whereas atoms are a familiar part of the scientific world, the true nature of the void between them is something that is still not fully understood and many scientists believe that the void question lies at the heart of all the “big” questions about the universe and the nature of reality. It is a question that nanotechnology can address, and we will return to this discussion in Chapter 8.

Meanwhile returning to atoms, one could argue that the basic philosophy outlined above, which led to their being proposed, means that you should really attribute the *a-tomon* to more fundamental constituents of atoms, such as electrons and quarks. There is a good reason to stick with atoms, however, since we are talking about constituents of materials; and if we pick on a particular material, say copper, the smallest indivisible unit of "copperness" is the copper atom. If we divide a copper atom in two, we get two atoms of different materials.

So what has all this got to do with nanotechnology? Nowadays we can carry out, in practice, the Democritus mind experiment and study pieces of matter of smaller and smaller size right down to the atom. The important result is that the properties of the pieces start to change at sizes much bigger than a single atom. When the size of the material crosses into the "nanoworld" (Fig. 0.1), its fundamental properties start to change and become dependent on the size of the piece. This is, in itself, a strange thing because we take it for granted that, for example, copper will behave like copper whether the piece is a meter across or a centimeter across. This is not the case in the nanoworld, and the onset of this strange behavior first shows up at the large end of the nanoworld scale with the magnetic properties of metals such as iron. It is worth spending a little time on this because it is a clear illustration of how the behavior of a piece of material can become critically dependent on its size.

1.2 THE MAGNETIC BEHAVIOR OF NANOPARTICLES

It is widely known that iron is a magnetic material, but in fact a piece of pure (or "soft") iron is not magnetized. This is easy to prove by taking a piece of soft Fe and seeing that it does not attract a ball bearing (Fig. 1.3a). In contrast, a permanent magnet, which is an alloy, such as neodymium–iron–boron that is permanently magnetized, strongly attracts the ball bearing (Fig. 1.3b). A simple and illustrative experiment is to sandwich the ball bearing between the permanent magnet and piece of soft iron and then pull the magnet and the pure iron apart (Fig. 1.3c). Oddly, while the ball bearing shows no attraction to the soft iron on its own, in the presence of the magnet it stays glued firmly to the piece of soft iron as it is pulled away, showing that it is magnetized to a greater degree than the actual magnet. Beyond a certain distance from the magnet, the soft iron reverts to its demagnetized state and the ball bearing comes loose (Fig. 1.3d).

The source of magnetism in materials is their constituent atoms, which consist of tiny permanent dipolar magnets whose strength is given by the *magnetic moment*[1] of the atom (see Advanced Reading Box 1.1). In a material such as iron, there is a strong interaction (the exchange interaction) between the atoms

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[1] Magnetic moment or magnetic dipole moment, denoted by the symbol μ, summarizes the characteristics of a simple loop of current, producing a magnetic field, by the equation $\mu = IA$, where I is the circulating current and A is the area enclosed by the loop. A simple loop such as this produces a *dipolar* magnetic field similar to that produced by a bar magnet with *north* and *south* poles.

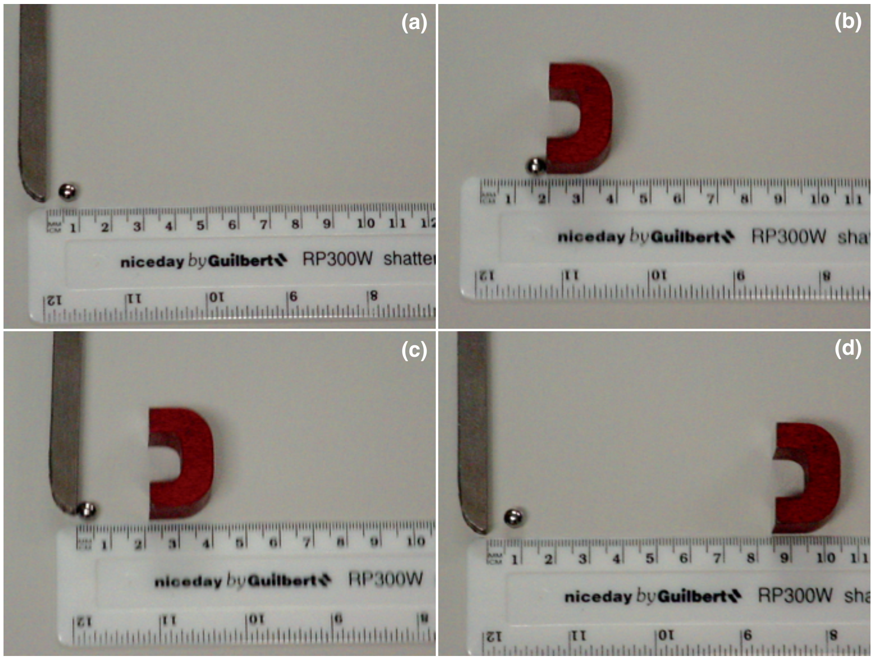

Fig. 1.3 Simple experiment to demonstrate magnetic domains. (a) Soft iron does not attract the ball bearing. (b) A conventional magnet does, however (c) when the soft iron is magnetized by being in the presence of the magnet it becomes more magnetic than the magnet and the ball bearing stays with the soft iron in preference to the magnet. (d) The situation persists until the magnet is far enough away that the soft iron reverts to its domain structure and externally generates no magnetic field.

that lines up the atomic magnets to produce a macroscopic magnetization. Note that the exchange interaction is a quantum mechanical effect and is not the normal interaction that you would see between two bar magnets, for example. For one thing the interaction between bar magnets aligns them in opposite directions, and for another the exchange interaction is thousands of times stronger than the direct magnetic interaction.

ADVANCED READING BOX 1.1—ATOMIC MAGNETIC MOMENTS AND THE EXCHANGE INTERACTION

The individual atoms of most elements have a permanent magnetic moment, so they generate a dipolar magnetic field similar to a simple bar magnet. The source of the atomic magnetic moment is twofold. It arises from the orbital motion of the electrons around the nucleus, which can be considered to constitute a simple current loop, and also from the intrinsic angular momentum (spin) of the electrons. These two contributions generate an orbital and a spin magnetic moment; and for the elements Fe, Co, and Ni, the two contributions are simply added to obtain the total magnetic moment. The exchange interaction that acts between neighboring atoms arises from the Pauli Exclusion Principle. This tends to keep electrons apart if they have the same spins so that the Coulomb repulsion energy between the outermost electrons of neighboring atoms is reduced if the electrons align their spins in the same direction. This appears as a very strong magnetic interaction trying to align the spin magnetic moments, but it is an electrostatic effect produced by the quantum nature of the electrons. It is typically 3–4 orders of magnitude stronger that the direct magnetic interaction of the atomic magnetic moments taken to be simple bar magnets.

So in a magnetic material the powerful exchange interaction tries to line up all the microscopic atomic magnets to lie in the same direction. This, however, is not necessarily the preferred configuration because the uniformly magnetized state generates a magnetic field that passes through the material and the magnetization finds itself pointing the wrong way in its own magnetic field; that is, it has the maximum *magnetostatic* energy.[2] Of course, reversing the magnetization is of no use because the generated field reverses and again the sample magnetization and the generated field are aligned in the least favorable direction to minimize energy. The exchange interaction and the magnetostatic energy are thus competing, which at first glance does not appear to be much of a competition considering that the exchange energy per atom between nearest neighbors is 3–4 orders of magnitude stronger than magnetostatic one. The magnetostatic interaction, however, is long range while the exchange interaction only operates between atomic neighbors. There is thus a compromise that will minimize the energy relative to the totally magnetized state by organizing the magnetization into so-called *domains* with opposite alignment (Fig. 1.4a). If these domains have the right size, the reduction in magnetostatic energy is greater than the increased exchange energy from the atoms along the boundaries that are neighbors and have their magnetization pointing in opposite directions. In the minimum energy state the material does whatever is necessary to produce no external magnetic field, and this is what has happened in Fig. 1.3a. The magnetization of the soft iron has organized itself into domains, and externally it is as magnetically dead as a piece of copper. The actual magnet has been treated to prevent the domains forming so that it stays magnetized (Fig. 1.3b). When we bring the piece of soft iron into the field of the magnet, its domains are all aligned in the same direction and it has a greater magnetization than the magnet so that when we pull the two apart, the ball bearing stays stuck firmly to the soft iron. This continues until the soft iron is far enough away from the magnet to revert to its domain structure and become magnetically dead externally.

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[2] Magnetostatic energy is the energy of a permanent magnet interacting with a static magnetic field.

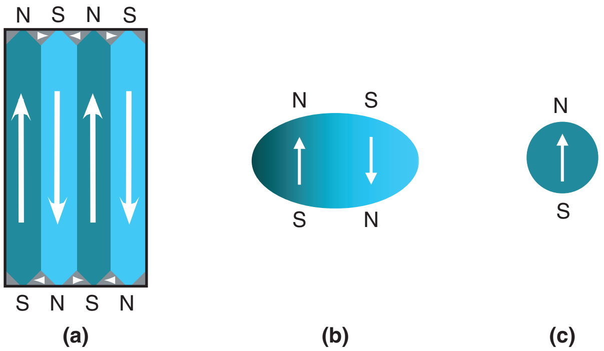

Fig. 1.4 Single-domain particles. Domain formation in iron to minimize energy. Below a critical size (approx. 100 nm), the energy balance favors just a single domain and the piece of iron stays permanently and fully magnetized.

The phrase "*If these domains have the right size*" in the previous paragraph encapsulates the critical point. If we do the Democritus experiment and start chopping the piece of soft iron into smaller and smaller pieces, the number of domains within the material decreases (Fig. 1.4b). There must come a size, below which the energy balance that forms domains simply does not work any more and the particle maintains a uniform magnetization in which all the atomic magnets are pointing the same way (Fig. 1.4c). So what size is this? It turns out to be about 100 nm—that is, the upper edge of the nanoworld. Any iron particle that is smaller than this is a single domain and is fully magnetized. This may seem like a subtle size effect, but it has profound consequences. Fully magnetized iron is a much more powerful magnet than any actual magnet as shown in Fig. 1.3. The reason is that a permanent magnet must contain some nonmagnetic material to prevent the process of domain formation so that its magnetization is diluted compared to the pure material. A world in which every piece of iron or steel was fully magnetized would be very different from our familiar one. Every steel object would attract or repel every other one with enormous force. Cars with their magnetization in opposite directions would be very difficult to separate if they came into contact.

Nature makes good use of this magnetic size effect. Bacteria, such as the one shown in Fig. 1.5, have evolved, which use strings of magnetic nanoparticles to orient their body along the local magnetic field lines of the Earth. The strain shown in the figure, which is found in northern Germany, lives in water and feeds off sediments at the bottom. For a tiny floating life form such as this, knowing up and down is not trivial. If the local field lines have a large angle to the horizontal, as they do in Northern Europe, then the string of magnetic nanoparticles makes the body point downwards and all the bacterium has to do is to swim knowing that it will eventually find the bottom.

The intelligence of evolution is highlighted here. If the particles are single-domain particles, then they will stay magnetized forever, so forming a string of

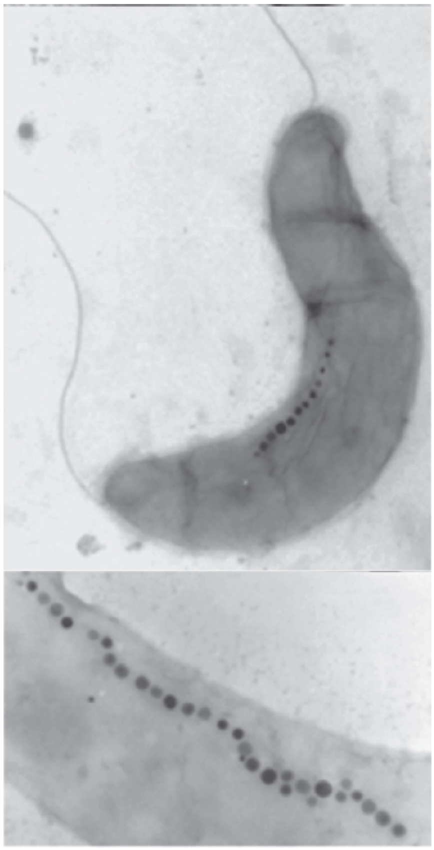

Fig. 1.5 Magnetic bacterium using single-domain particles. The Magnetic bacterium (*magnetospirillum gryphiswaldense*) from river sediments in Northern Germany. The lines of (permanently magnetized) single-domain magnetic nanoparticles, appearing as dark dots, align the body of the bacterium along the local direction of the Earth's magnetic field, which in Germany is inclined at 55° from horizontal. This means that the bacterium will always swim downwards towards the sediments where it feeds. Reproduced with With kind permission of Springer Science and Business Media from D. Schüler [2].

these ensures that the navigation system will naturally work. If the bacterium formed a single piece of the material the same size as the chain of particles, then a domain structure would form and it would become magnetically dead. The nanoparticles are composed of magnetite (Fe_3O_4) rather than pure iron, but the argument is the same. There is currently research devoted to persuading the bacteria to modify the composition of the nanoparticles by feeding them with cobalt-containing minerals as a method of high-quality nanoparticle synthesis (see Chapter 4, Section 4.1.8).

Interestingly, chains of magnetic nanoparticles with a similar structure have been found on a piece of meteorite known to have come from Mars [3]. Since

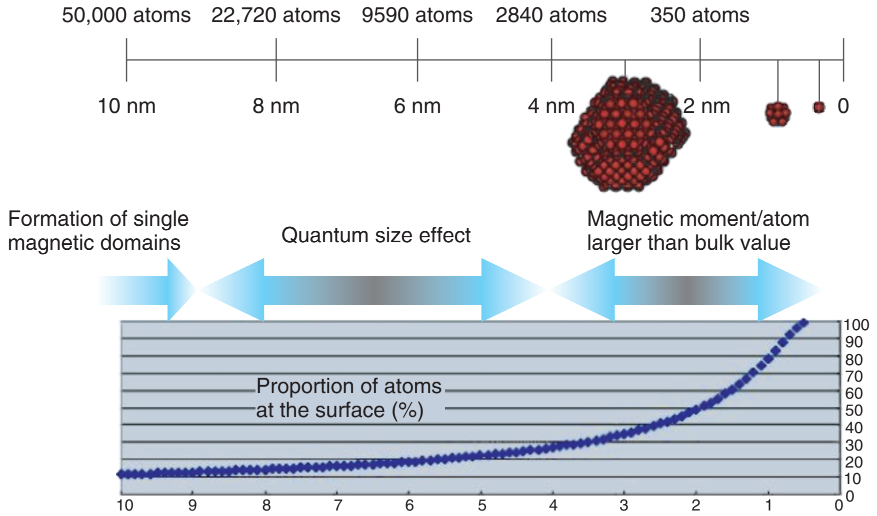

Fig. 1.6 Size-dependent behavior in nanoparticles. For particles smaller than 10 nm, quantum effects start to become apparent. In this size range the proportion of atoms that constitute the surface layer starts to become significant reaching 50% in 2 nm diameter particles. Below about 3 nm the strength of magnetism per atom starts to increase.

the only known way of producing this mineral is biological, the observation is evidence that there was once life on Mars, though this analysis remains controversial. In fact, Mars no longer has a significant planetary magnetic field, which disappeared in the distant past, but supporters of the Martian bacteria proposal argue that there could be localized magnetic fields around magnetic minerals on the surface.

Formation of single-domain particles is only the onset of size effects in the nanoworld. If we continue the Democritus experiment and continue to cut the particles into smaller pieces, other size effects start to become apparent (Fig. 1.6). In atoms the electrons occupy discrete energy levels, whereas in a bulk metal the outermost electrons occupy energy bands, in which the energy, for all normal considerations, is a continuum. For nanoparticles smaller than 10 nm, containing about 50,000 atoms, the energy levels of the outermost electrons in the atoms start to display their discrete energies. In other words, the quantum nature of the particles starts to become apparent. In this size range, a lot of the novel and size-dependent behavior can be understood simply in terms of the enhanced proportion of the atoms at the surface of the particles. In a macroscopic piece of metal—for example, a sphere 2 cm across—only a tiny proportion of the atoms, less than 1 in 10 million, are on the surface atomic layer. A 10-nm-diameter particle, however, has 10% of its constituent atoms making up the surface layer, and this proportion increases to 50% for a 2-nm particle. Surface atoms are in a chemical environment that is different from that of the interior and are either exposed to vacuum or interacting with atoms of a matrix in which the

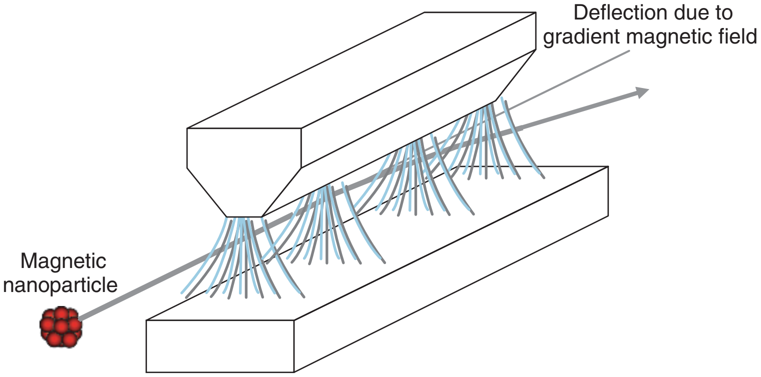

Fig. 1.7 Measuring the magnetic moment in free nanoparticles. The magnetic moment in free nanoparticles can be measured by passing a beam of them through a non-uniform magnetic field and measuring the deflection in their path.

nanoparticle is embedded. Novel behavior of atoms at the surfaces of metals has been known for decades; thus, for example, the atomic structure at the surface is often different from that of a layer in the interior of a bulk crystal. When such a high proportion of atoms comprise the surface, their novel behavior can distort the properties of the whole nanoparticle.

Returning to magnetism, a well-known effect in sufficiently small particles is that not only are they single domains but also the strength of their magnetism per atom is enhanced. A method for measuring the strength of magnetism (or the *magnetic moment*) in small free particles is to form a beam of them (see Chapter 4, Section 4.1.1 for a description of nanoparticle sources) and pass them through a nonuniform magnetic field as shown in Fig. 1.7. The amount the beam is deflected from its original path is a measure of the nanoparticle magnetic moment; and if the number of atoms in the particles is known, then one obtains the magnetic moment per atom.

Magnetic moments of atoms are measured in units called Bohr magnetons[3] or μ_B (after the Nobel laureate Neils Bohr), and the number of Bohr magnetons specifies the strength of the magnetism of a particular type of atom. For example, the magnetic moments of iron, cobalt, nickel, and rhodium atoms within their bulk materials are $2.2\mu_B, 1.7\mu_B, 0.6\mu_B$, and $0\mu_B$ (rhodium is a nonmagnetic metal), respectively. Figure 1.8 shows measurements of the magnetic moment per atom in nanoparticles of the above four metals as a function of the number of atoms in the particle. In the case of iron, cobalt, and nickel, a significant increase in the magnetic moment per atom over the bulk value is observed for particles containing less than about 600 atoms. Perhaps most surprisingly, sufficiently

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[3] A Bohr magneton (1 μ_B) is the magnetic moment of a single free electron produced by its intrinsic angular momentum (spin).

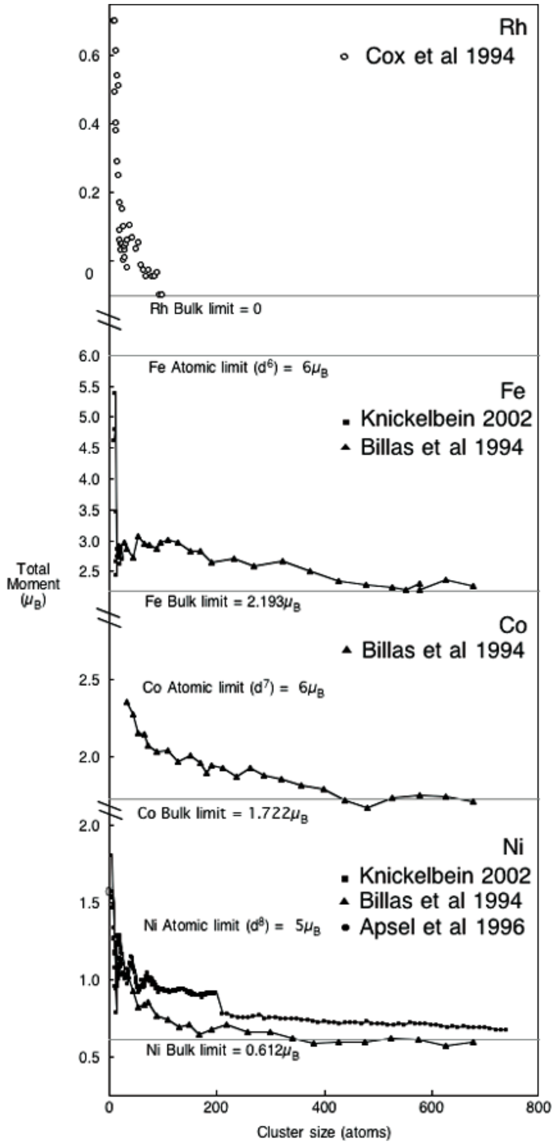


Fig. 1.8 Measured magnetic moments per atom in magnetic nanoparticles. Experimental measurements of the magnetic moment per atom in iron, cobalt, nickel and rhodium (a non-magnetic metal in the bulk) nanoparticles as a function of the number of atoms in the particle. For iron, cobalt and nickel, there is a significant increase in the magnetic moment per atom over the bulk value for particles containing less than about 600 atoms. Rhodium becomes magnetic in particles containing less than about 100 atoms. Note the very dramatic change in the magnetic moment of iron particles in going from a 12-atom particle to a 13-atom particle. Reproduced with the permission of the American Association for the Advancement of Science (AAAS) from I. M. L. Billas et al. [4], permission of the American Physical Society from A. J. Cox et al. [5] and S. Apset et al. [6], Copyright 1994 and 1996 and permission of Elsevier Science from M. B. Knickelbein [7].

small particles (containing less than about 100 atoms) of the nonmagnetic metal rhodium become magnetic.

Throughout the whole size range in Fig. 1.8, the fundamental magnetic behavior of the particles is size-dependent. Do not lose sight of how strange a property this is and how it runs counter to our experience in the macroscopic world. It is as strange as a piece of metal changing color if we cut it in half (something else that happens in nanoparticles). If Democritus were doing his chopping experiment on iron, when he reached a piece 100 nm across, which would be invisible in even the most powerful optical microscope, he would say that he had not yet reached the *atomon* because up to then there would have been no observable change in properties. When he cut in half again, he would suddenly find his piece changing from showing no external magnetism to the full magnetic power of iron with every atomic magnet aligned as the piece formed a single domain particle. He would exclaim "I have reached the *atomon*, let's just try and cut again" (he has nanoscale scissors of course). Imagine his surprise when he finds he can continue and on reaching 3 nm finds that when he cuts again the strength of the magnetism, in proportion to the size of the piece, increases. Is this new piece the *atomon*? Well no, because from then on he would get a change in properties whenever he cut. Some of these changes can be dramatic. For example, if he was holding a 13-atom cluster (let us assume we know what an atom is) and shaved off a tiny piece to produce a 12-atom cluster, the magnetic moment per atom would jump from $2.5\mu_B$ to a staggering $5.5\mu_B$—very close to the single-atom limit of $6\mu_B$.

This highlights one of the most exciting aspects of nanoparticle research. If one considers a nanoparticle as a building block and can assemble large numbers of them to make a material, then it is possible to tailor the fundamental properties of the building block just by changing its size. In Chapter 5 we will look at more sophisticated ways of changing the nanoparticle building blocks. The ability to change the fundamental properties of the building blocks will surely enable us to produce new high-performance materials. As an example, if we deposit iron onto a surface to make a thin film, there is a difference between depositing individual atoms, as with a conventional evaporator, and depositing whole nanoparticles containing, say, 200 atoms. This is clear from Fig. 1.9, which shows a thin film of iron produced by depositing nanoparticles onto a silicon substrate in vacuum. It is clearly a random stack of the deposited particles showing that they have not coalesced to form a smooth film. On this scale a film of the same thickness produced by depositing atoms would appear smooth and featureless, and it would behave differently than the nanoparticle stack.

It is becoming clear that making magnetic thin films out of magnetic nanoparticles may be a way of producing more powerful magnetic materials. First of all, it is worth pointing out that finding a material with an enhanced magnetism per atom over the most magnetic conventional material we have available (iron–cobalt or "permendur" alloy) is regarded as a hugely difficult problem. It has been recognized since 1929 that iron–cobalt alloys have the highest magnetization of all magnetic alloys [9], and materials scientists have been looking for a magnetic

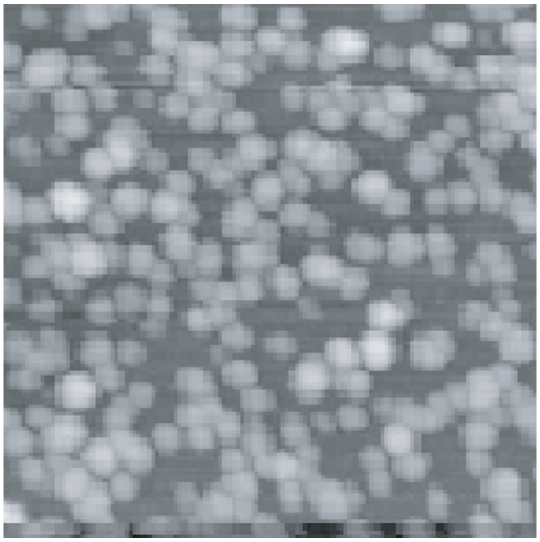


Fig. 1.9 Morphology of nanoparticle film. STM image (see Chapter 4, Section 4.4.1) with an area of 100 nm × 100 nm of thin film produced by depositing 3 nm diameter iron nanoparticles onto a silicon substrate in vacuum. It is clearly a random stack of the deposited particles and the film properties will be different to those of a smooth film that would be formed by depositing iron atoms. Reproduced with the permission of the American Institute of Physics from M. D. Upward et al. [8].

material with a yet higher performance ever since. Finding such a material would be an important discovery in technology generally. Magnetic materials form a kind of invisible background to our technological existence that we hardly notice, but they are all-pervasive. A useful exercise is to count the number of magnets in one's car, for example. Including all the motors, sensors, and the entertainment system, there will be dozens.

Making high-performance materials is hinted at by the data in Fig. 1.8, which reveal significant increases in magnetism per atom in magnetic nanoparticles. Unfortunately, simply spraying large numbers of iron nanoparticles onto a surface to produce a thick version of the film shown in Fig. 1.9 does not work. The particles in the film would maintain an enhanced magnetic moment per atom but the film is porous, containing a lot of nanoscale voids. The overall performance of the material is a weighted average of the particles and voids; and such a film would have an average magnetic moment per unit volume less than bulk iron, never mind bulk permendur. This is not the end of the story, however, since we can fill the voids by depositing the particles at the same time as a vapor of atoms from a conventional evaporator as shown in Fig. 1.10 [10]. The nanoparticles become embedded in the film (or matrix) produced by the atoms to produce a kind of nanoscale *plum pudding* where the nanoparticles are the plums and the atoms form the pastry. This kind of film is no longer porous and has a density

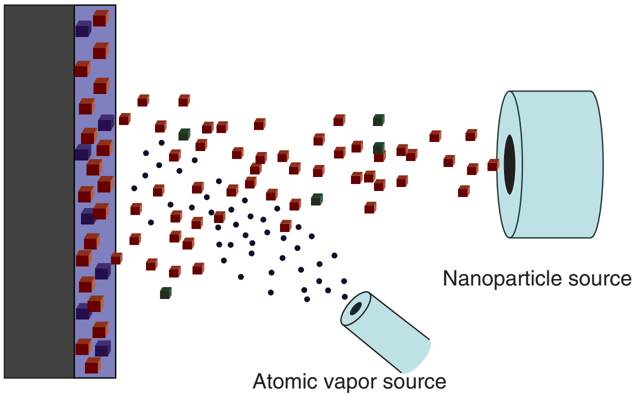
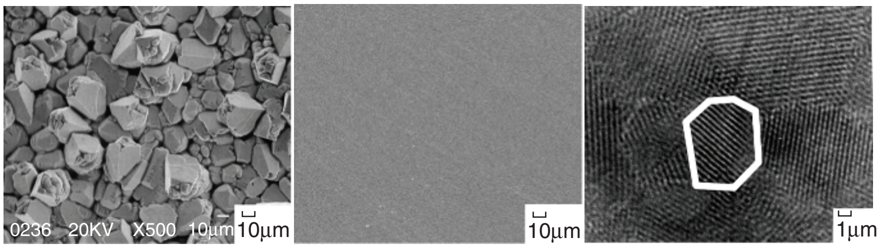


Fig. 1.10 Making granular materials by co-depositing nanoparticles and atoms. A granular material with nanoscale grains can be produced by co-depositing Pre-formed nanoparticles with an atomic vapor from a conventional evaporator. The nanoparticles are embedded in a matrix produced by the atomic vapor to form a granular material in which there is independent control over the volume fraction and grain size.

close to the value found for the bulk materials. If the nanoparticles are iron and the matrix is cobalt (or vice versa), then this method forms a granular version, with nanoscale grains, of the permendur alloy, which has been shown to produce a material with a higher magnetization than conventional permendur [11].

1.3 THE MECHANICAL PROPERTIES OF NANOSTRUCTURED MATERIALS

Mechanical properties such as the strength of metals can also be greatly improved by making them with nanoscale grains. Several basic attributes of materials are involved in defining their mechanical properties. One is strength, which includes characteristics with more precise definitions but basically determines how much a material deforms in response to a force. Others are (a) hardness, which is given by the amount another body such as a ball bearing or diamond is able to penetrate a material, and (b) wear resistance, which is determined by the rate at which a material erodes when in contact with another. These properties are dominated by the grain structure found in metals produced by normal processing. An example of the grains structure of a "normal" piece of metal is shown in Fig. 1.11a, which is an electron microscope image showing the grain structure of tin. Each grain is a single crystal with a typical size of about 20 μm (20,000 nm). The mechanical properties listed above are due to grains slipping past each other or deforming, so clearly what happens at the grain boundaries is very important in determining properties such as strength. By using various techniques including nanoparticle deposition (Fig. 1.10), electrodeposition, and special low-temperature milling methods, it is possible to produce metal samples in which the



(a) (b) (c)

Fig. 1.11 Grain size in nanostructured materials. Electron microscope images showing a comparison of the grain structure in conventional and nanostructured materials. (a) Conventionally processed material (tin) showing a typical grain size of about 20 µm. (b) Nanovate™ nanostructured nickel based coating produced by Integran Technologies Inc. On the same scale as (a) the material appears homogenous. (c) Increasing the magnification by a factor of 15,000 reveals the nano-sized grains. The lines in the picture are atomic planes and the edges of the grains are revealed by changes in the direction of the planes as indicated for one of the grains. Reproduced with permission from Integran Technologies Inc. (http://www.integran.com).

grains are a few nanometers across. An example is shown in Fig. 1.11b, where, on the same scale as Fig. 1.11a the grain structure disappears to show a homogeneous material. Blowing up the magnification a further 15,000×, however (Fig. 1.11c), reveals the new nanoscale grain structure. In this image the individual planes of atoms are indicated by the sets of parallel lines, and the boundaries are where the lines suddenly change direction as indicated for one of the grains. Whereas in the coarse-grained metal shown in Fig. 1.11a, about one atom in 100,000 is at a grain boundary, in the nano-grained equivalent, about a quarter of the atoms are at a grain boundary. Clearly this change is going to have a marked effect on the mechanical properties of the material. Changes in mechanical properties with grain size were quantified over 50 years ago by Hall and Petch [12, 13], but the modern ability to vary the grain size right down to the nanometer scale is likely to yield large increases in performance.

The most dramatic improvement is seen in the "yield strength," which quantifies the load a material can tolerate before it becomes permanently deformed. All metals are elastic under a small load; that is, when the load is removed, they return to their original shape, while beyond a certain load they deform plastically and remain permanently changed. Figure 1.12 [14] shows a plot of the strain (relative elongation of a sample) versus stress (load) for various nanostructured aluminum alloys compared to normal (coarse-grained) aluminum alloy. The plastic limit or yield strength occurs at the point where the slope changes, and it is seen that nanostructured materials have a value that is up to four times higher that the conventional material. This is a dramatic increase in strength, but even higher values have been found in other metals—for example, a 10-fold increase in copper [15]. A problem with nanostructured materials is also revealed by the

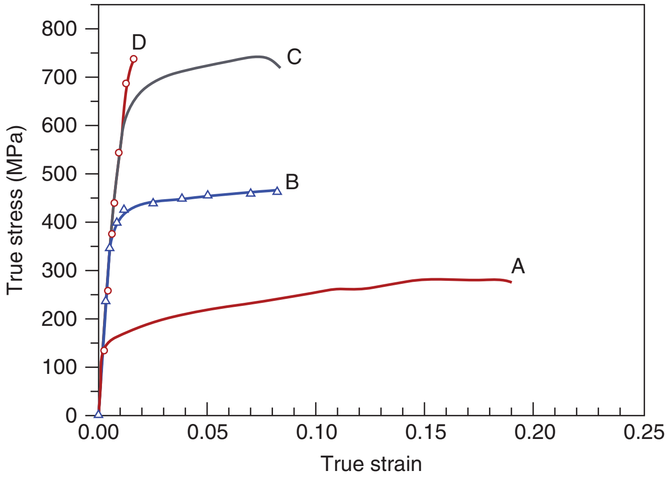


Fig. 1.12 Yield strength of aluminium alloys. Comparison of Deformation (Strain) vs. Load (Stress) for aluminium alloys with different grain sizes. A normal aluminium alloy (coarse-grained). $B - D$ nanostructured aluminium alloy containing grains of size ∼30 nm produced by various processes. The plastic limit occurs at the point where the slope changes and the nanostructured materials have a value that is up to four times higher that the conventional alloy. Reproduced with the permission of Elsevier Science from K. M. Youssef et al. [14].

plot, however; that is, they fail (break) at relatively low strains. Problems such as this are being addressed by improvements in processing [15].

1.4 THE CHEMICAL PROPERTIES OF NANOPARTICLES

Another size-dependent property of nanoparticles is their chemical reactivity. This is demonstrated most dramatically by gold, which in the bulk is the archetypal inert material. This is one of the reasons why it is so highly valued since it does not corrode or tarnish and thus has a timeless quality. The only acid that is known to attack it is a hellish brew of concentrated nitric and hydrochloric acids mixed to form what has been poetically named aqua regia (royal water). It would therefore seem that gold, would be useless as a catalyst to speed up chemical reactions, but this is not so for gold nanoparticles. In fact, most catalysts are in the form of nanoparticles; and bearing in mind everything that has been said so far about how material properties change with size in the nanoworld, the same is true of gold. When gold is in the form of nanoparticles with diameters less than about 5 nm, it becomes a powerful catalyst, especially for the oxidation of carbon monoxide (CO). The full story is quite complicated because the reactivity of gold nanoparticles appears to depend not only on their size but also on the material on which they are supported.

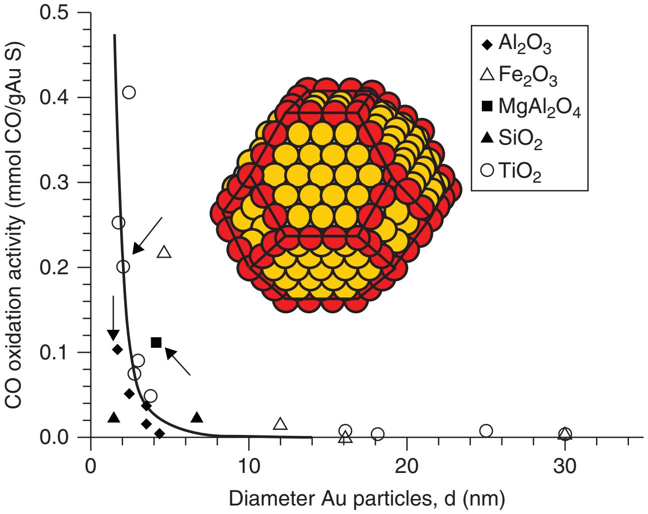


Fig. 1.13 Reactivity of gold nanoparticles. Measured activities of gold nanoparticles on various supports (box) for carbon monoxide oxidation as a function of particle size. The black line is a fit using a $1/d^3$ law and is seen to broadly represent the variation indicating that the dominant effect size effect is the proportion of gold atoms that are at a corner between facets at the surface (see text). Such atoms are highlighted in red on the nanoparticle shown. Reproduced with the permission of Elsevier Science from N. Lopez et al. [16].

A recent assessment of a number of research papers on the effectiveness of gold in catalyzing the above reaction, however [16], has concluded that the dominant effect is that of the gold nanoparticle size, with the nature of the support playing a secondary role. Figure 1.13 shows a compilation of data on the carbon monoxide (CO) oxidation activity of gold nanoparticles on various supports as a function of their size and shows the impressive performance of the gold, which is completely inert in macroscopic-sized pieces. Since catalysis can only occur at the surface layer of atoms, the dominant size effect is the proportion of gold atoms that are at the surface. In fact the most important atoms for catalysis are those at the corners between different facets. These low coordinated atoms are where the reacting carbon monoxide (CO) molecules preferentially bond to during the reaction. The fraction of this type of atom (highlighted in red in Fig. 1.13) is proportional to $1/d^3$, where d is the particle diameter and the black line in Fig. 1.13 is a fit to the data using this law demonstrating that the dominant size effect is indeed the proportion of corner atoms at the surface. The focus here has been on gold because of its extreme demonstration of size-dependence—that is, from a completely inert material to a powerful catalyst—but as a general rule the performance of all catalysts depends on the particle size. Because of the importance of catalysts to the chemical industry, the effect is the focus of a large amount of research activity.

1.5 NANOPARTICLES INTERACTING WITH LIVING SYSTEMS

The novel properties of nanoparticles—for example, the enhanced chemical reactivity—makes their interaction with biological systems dependent on particle size. This can be illustrated with the example of silver nanoparticles. It has been known for some time that silver is highly toxic to a wide range of bacteria, and silver-based compounds have been used extensively in bactericidal applications. This property of silver has caused great interest, especially because new resistant strains of bacteria have become a serious problem in public health. For example, MRSA bacteria kill 5000 hospital patients a year in the United Kingdom alone; and any method of attacking them, not involving normal antibiotics, is becoming increasingly important. Trials of silver-loaded wound dressings and special fabric with silver yarn woven into it have proved highly successful in treating and preventing the spread of MRSA infections [17]. There is also interest from less urgent but nevertheless important applications such as slow release of silver from compounds for preservatives or long-lasting bactericidal protection in plastics.

Silver in the form of nanoparticles becomes yet more effective, partly because of the high surface/volume fraction so that a large proportion of silver atoms are in direct contact with their environment. In addition, nanoparticles are sufficiently small to pass through outer cell membranes and enter cells' inner mechanisms. A recent study using nanoparticles with a wide size range [18] showed that only silver nanoparticles with sizes in the range 1–10 nm were able to enter cells and disrupt them. They were found to do this in two ways. Some particles attached to the cell membrane and disturbed its functions, such as respiration. Others penetrated the outer membrane and caused further damage, including damage to the cell DNA. Figure 1.14 shows an electron microscope image of some P. *aeruginosa*[4] bacteria after they had been exposed to silver nanoparticles, and the high magnification inset reveals some nanoparticles attached to the cell membranes. This strain can be particularly problematic to cystic fibrosis sufferers because it readily colonizes the favorable environment found in their lungs. It protects itself by producing a thick mucus layer, which makes it difficult to treat with antibiotics once it is established. Silver nanoparticles suspended in an aerosol could prove to be an effective treatment.

There may also be some role for nanoparticles in the fight against AIDS. The same team that carried out the work described above also exposed the HIV-1 virus to silver nanoparticles of the same size [19]. There has been very little work on the interaction of nanoparticles with viruses, which are much smaller than bacteria and are themselves inhabitants of the nanoworld (see Fig. 0.1). It was discovered that, again, the important size range is 1–10 nm; and, as shown in Fig. 1.15, nanoparticles of this size attached themselves in an ordered array on the surface of the virus. The HIV-1 virus is covered in a regular arrangement

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[4] Bacterium that infects the lungs of cystic fibrosis sufferers and causes inflammation and breathing problems.

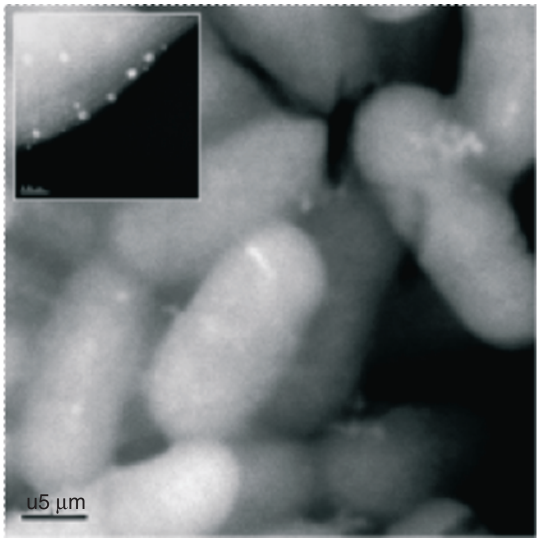

Fig. 1.14 Silver nanoparticles attacking bacteria. Electron microscope image of P.aeruginosa[4] bacteria after exposure to silver nanoparticles. The particles with size ranges 1 – 10 nm are active in disrupting the cell function. The inset shows a high-resolution image of some particles attached to the cell outer membrane. Reproduced with the permission of the Institute of Physics from J. R. Morones et al. [18].

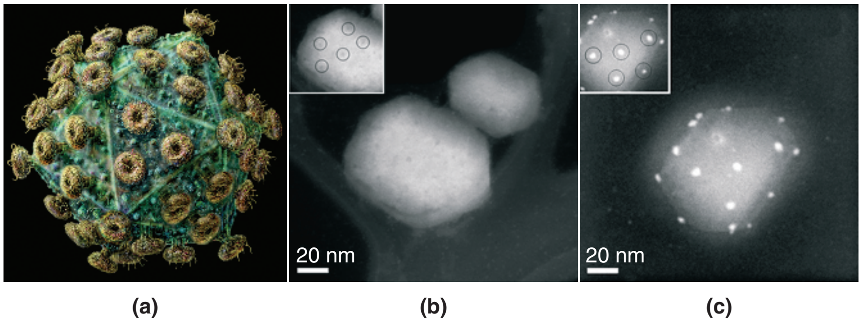

Fig. 1.15 Silver nanoparticles attached to HIV-1 virus. (a) Computer generated image of HIV virus, showing glycoprotein ‘knobs’ (Reproduced with permission from www.virology.net/Big_Virology/BVretro.html). (b) Electron microscope image, with inset superimposing position of knobs. (c) Electron microscope image of virus after attachment of silver nanoparticles. Reproduced with the permission of BioMed Central from J. L. Elechoguerra et al [19].

of glycoprotein “knobs” (Fig. 1.15), and the average distance between the silver nanoparticles in the image suggests that they attach themselves to these knobs. The team went on to demonstrate that the nanoparticles prevent the virus from binding to host cells.

Here we have only encountered very brief sketches of a couple of examples of applications of nanoparticles in health care. This is a huge and burgeoning field, and a more comprehensive discussion is postponed until Chapter 6. As a final example in this chapter, it is worth noting that there is increasing use of nanoparticles in cosmetics such as face creams. In order to replenish certain compounds in the skin, whose reduced concentration is partly responsible for the effects of aging, it is necessary to enable these compounds to penetrate the outermost layers of skin. This can mean either producing the compounds themselves as nanoparticles or binding them onto “carrier” particles that transport them to the deeper layers. Some sunscreen manufacturers now use titanium dioxide nanoparticles in new products as the carriers.

The key aims of this chapter have been to give an impression of the nanometer size scale and to introduce the idea that sufficiently small pieces of matter behave differently than the bulk material. In addition, the novel behavior of nanoparticles depends on their size, and several examples have been introduced where the unusual behavior can be put to good use in technology. All the topics discussed fall into the category of incremental nanotechnology, and it is evident that this category is already being used or will shortly be used in industrial sectors ranging from magnetic recording to medicine. All the types of nanoparticle presented here are artificially produced; but in the following chapter, naturally occurring nanoparticles and their effect on the environment and our health will be discussed.

PROBLEMS

1. Silver, whose density is 10,490 kg/m^3, is used to form spheres of different diameters. Calculate the surface area in m^2 of 1 g of Ag spheres of diameter:
   (a) 1 mm
   (b) 10 μm
   (c) 10 nm

2. Calculate the proportion of atoms on the surface atomic layer of Ag spheres with the diameters below given that the thickness of the surface atomic shell is 0.289 nm, stating any assumptions made.
   (a) 1 μm
   (b) 10 nm
   (c) 5 nm

3. In a magnetic material the energy of the exchange interaction between neighboring atoms is about 1 eV/atom, whereas the magnetic dipolar interaction between neighboring assemblies of atoms has an average value of 10^{-5}

eV/atom. Use this data to estimate the maximum size of a spherical single-domain particle. (*Hint*: Assume that the exchange interaction only operates between atomic neighbours, whereas in a small particle the dipolar interaction affects all atoms equally. In addition, for an estimate, assume that the atoms are cubes with a width of 0.2 nm.[5])

4. An HIV virus with a diameter of 100 nm has 50 glycoprotein extrusions over its surface, each one of which will bind a 5-nm-diameter Ag nanoparticle. You are provided with a suspension of 5-nm-diameter Ag nanoparticles containing 1 μg Ag per milliliter of liquid. What volume of the suspension is required to saturate 10^7 viruses in a test tube?

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[5] You should find that your estimate is much larger than the critical size (∼100 nm) for a single domain particle given in the text. The reason is that the exchange energy in a domain boundary can be reduced by a large factor by spreading it over a number of atomic layers. That is, instead of having an abrupt 180° reversal of the magnetization across a single atomic plane, the magnetization rotates a fraction of 180° across each plane. This brings the critical size down to ∼100 nm).

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