1

Size Matters

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 round 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 it has been defined as the distance 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 Figure I.1 in the introduction ("The Nanoworld"), we will be dealing with building blocks that vary from 100 nm across down to atoms, which are 0.1–0.4 nm across.

These days instruments can directly image nanostructures, for example, Figure 1.1 shows a scanning tunneling microscope (STM – see Chapter 5, Section 5.4.1) image of a few manganese nanoparticles with a diameter of about 3 nm 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 Figure 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.

It may seem odd to base an entire branch of science and technology around a measure of distance, especially as length scales used in science go to much smaller than nanometers and much larger than meters. This is illustrated in Figure 1.2, which shows the entire distance range

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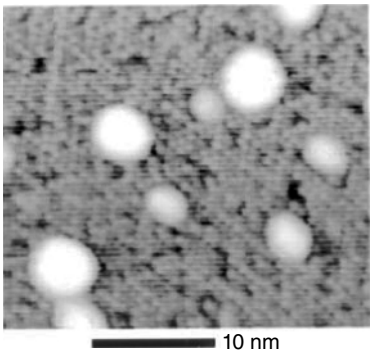

Figure 1.1 Manganese nanoparticles on bucky balls. STM image (see Chapter 5, Section 5.4.1) of a few manganese nanoparticles with a diameter of about 3 nm (i.e. each one contains a few hundred manganese atoms) deposited onto a bed of carbon-60 nanoparticles with a diameter of 0.7 nm on a silicon surface. *Source:* Reproduced with the permission of the American Institute of Physics from M. D. Upward et al. [1].

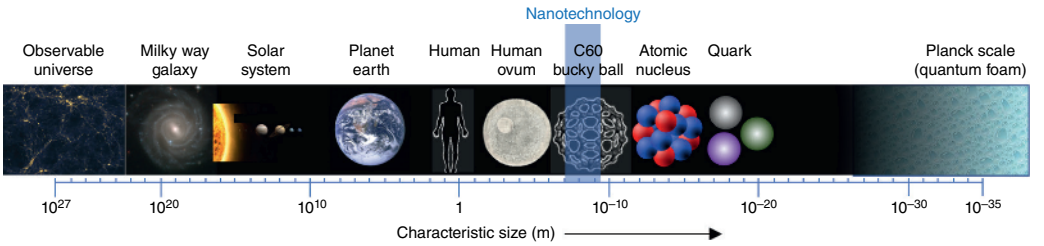

Figure 1.2 Distance range encompassing all current scientific knowledge. Distance scale from the observable Universe (10^{27} m) to the Planck scale (10^{-35} m) with nanoscience based on a narrow range near the middle. *Source:* The Universe image is from UCL Mathematical and Physical sciences and reproduced under creative commons 2.0 license. The solar system and atomic nucleus images are reproduced under creative commons 3.0 license.

encompassing present-day scientific knowledge, plotted on a logarithmic scale, from the observable universe (10^{27} m) to the Planck scale (10^{-35} m, see Chapter 10). It is seen that nanoscience occupies a tiny sliver somewhere near the middle and doesn't immediately strike one as being of interest, but to base a field of science around it suggests that there is something special about the nanometer scale – so what is it?

The answer to this is best expounded with reference to philosophical questions that were originally posed regarding the fundamental nature of matter and space by Democritus and his contemporaries that still resonate today. Democritus (Figure 1.3) was born in Abdera, Northern Greece, in about 460 BC 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 topics ranging from magnets to spiders and their webs. Only fragments of his work survived with most of his books being destroyed in the third and fifth centuries. His lasting impact on science was to propose, with his teacher Leucippus, the concept of the atom.

Our direct 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. In fact, there are subtle indications of underlying invisible particles of matter, for example, in a dusty room traversed by shafts of sunlight, the dust particles dance around due to the motion of something invisible. Mostly, this is microscopic air currents but the glittering of the smallest particles is due to random collisions from large numbers of individual air molecules and is known as Brownian motion (see Chapter 7, Section 7.2).

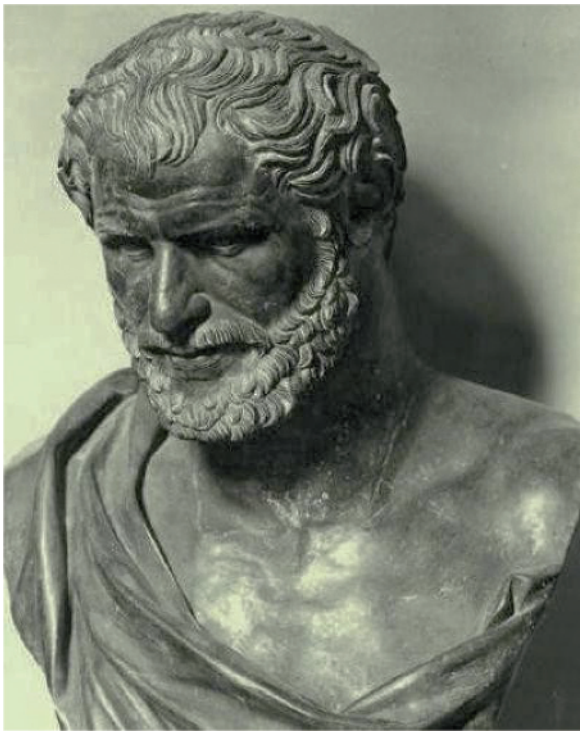

Figure 1.3 **Democritus.** Bronze bust thought to be of Democritus at the Naples National Archaeology Museum. *Source:* Odysses, https://commons.wikimedia.org/wiki/File:Bust_of_an_unknown_Greek_-_Museo_archeologico_nazionale_di_Napoli.jpg.

For the most part, matter does appear to be a continuum but this leads to a paradox since it could then 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*, or uncuttable from which the modern word *atom* is derived. They suggested the different substances in the world were composed of atoms of different shapes and sizes, which is not an unrecognizable 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 3000 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 subject that nanotechnology can address, and we will return to this discussion in Chapter 10.

Meanwhile, focusing on 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? These days 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" (Figure I.1), its fundamental properties start to change and become dependent on the size of the piece. This is, in itself, a strange thing as 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 (Fe). It is worth spending a little time on this because it is a clear illustration of how the fundamental behavior of a piece of material can become dependent on its size.

1.2 The Magnetic Behavior of Nanoparticles

It is widely known that Fe is a magnetic material, but in fact, a piece of pure (or "soft") Fe 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 (Figure 1.4a). In contrast, a permanent magnet, which is an alloy, such as neodymium–iron–boron (Nd–Fe–B) that is permanently magnetized strongly attracts the ball bearing (Figure 1.4b). A simple and illustrative experiment is to sandwich the ball bearing between the permanent magnet and piece of soft Fe, and then pull the magnet and the pure Fe apart (Figure 1.4c). Oddly, while the ball bearing shows no attraction to the soft Fe on its own, in the presence of the magnet it stays glued firmly to the piece of soft Fe as it is pulled away, showing that the soft Fe is magnetized to a greater degree than the actual magnet. Beyond a certain distance from the magnet the soft Fe reverts to its demagnetized state and the ball bearing comes loose (Figure 1.4d).

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 Fe, there is a strong interaction (the exchange interaction) between the atoms that line 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.

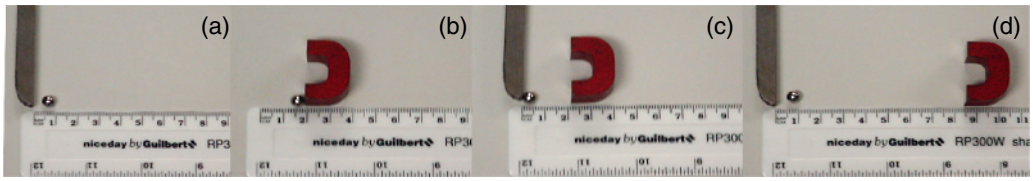

Figure 1.4 Simple experiment to demonstrate magnetic domains. (a) Soft Fe does not attract the ball bearing. (b) A conventional magnet does; however, (c) when the soft Fe is magnetized by being in the presence of the magnet, it becomes more magnetic than the magnet and the ball bearing stays with the soft Fe in preference to the magnet. (d) The situation persists until the magnet is far enough away that the soft Fe reverts to its domain structure and externally generates no magnetic field.

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.

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 than the direct magnetic interaction of the atomic magnetic moments assuming they are 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 the 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 (Figure 1.5a). 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 Figure 1.4a. The magnetization of the soft Fe 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 (Figure 1.4b). When we bring the piece of soft Fe 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 Fe. This continues until the soft Fe is far enough away from the magnet to revert to its domain structure and become magnetically dead externally.

The phrase "If these domains have the right size" in the previous paragraph encapsulates the essential point. If we do the Democritus experiment and start chopping the piece of soft Fe into smaller and smaller pieces, the number of domains within the material reduces (Figure 1.5b).

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

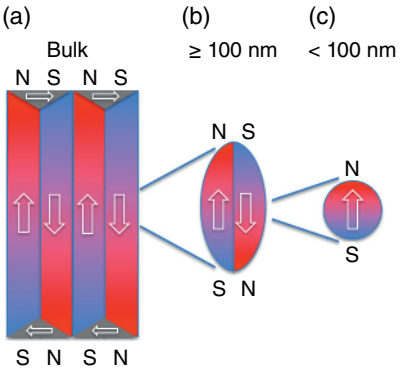

Figure 1.5 Single-domain particles. Domain formation in Fe to minimize energy. Below a critical size (approx. 100 nm), the energy balance favors just a single domain and the piece of Fe stays permanently and fully magnetized. Arrows show the direction of magnetization.

There must come a size, below which the energy balance that forms domains simply does not work anymore and the particle maintains a uniform magnetization in which all the atomic magnets are pointing in the same direction (Figure 1.5c). So what size is this? It turns out to be about 100 nm, that is, the upper edge of the nanoworld. Any Fe 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 Fe is a much more powerful magnet than any actual magnet as shown in Figure 1.4. 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 Fe 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 Figure 1.6 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 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, a domain structure would form and it would become magnetically dead. The nanoparticles are composed of magnetite (Fe_3O_4) rather than pure Fe 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 (Co)-containing minerals as a method of high-quality nanoparticle synthesis (see Chapter 5, Section 5.1.9).

Interestingly, magnetic nanoparticles with a similar atomic structure have been found on a piece of meteorite known to have come from Mars [3] and this was taken as evidence that there was once life on Mars, though this analysis is controversial. Mars no longer has a significant planetary magnetic field, which disappeared some four billion years ago indicating that the nanofossils, if that is what they are, must be truly ancient. There are, however, localized magnetic fields around magnetic minerals on the surface that could have been used by magnetic bacteria more recently, though still in the distant past.

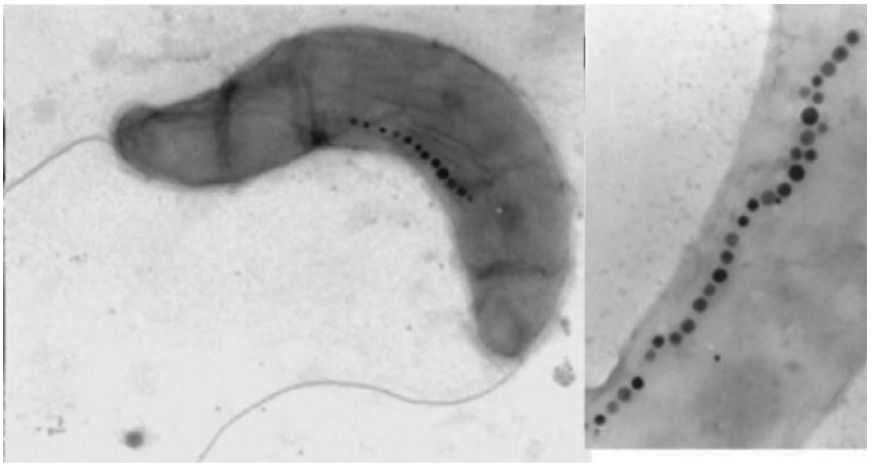

Figure 1.6 **Magnetic bacterium using single-domain particles.** The Magnetic Bacterium (*Magnetospirillum gryphiswaldense*) from river sediments in Northern Germany. The lines of (permanently magnetized) single-domain magnetic nanoparticles, appearing as dark dots, align the body of the bacterium along 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 downward toward the sediments where it feeds. *Source:* Reproduced with the permission of the Int. J. Microbiol. from D. Schüler [2].

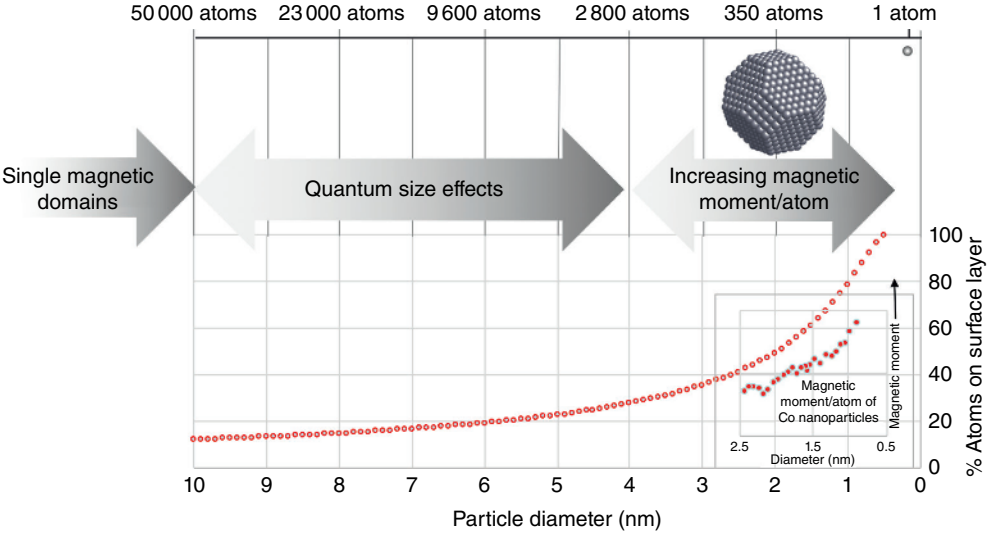

Figure 1.7 **Size-dependent behavior in nanoparticles.** For particles smaller than 10 nm, quantum effects start to become apparent. In this size range, the proportion of atoms that constitute the surface layer starts to become significant reaching 50% in 2 nm diameter particles. Below about 3 nm, the strength of magnetism per atom starts to increase as shown in the inset for measurements on Co nanoparticles (see text).

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 (Figure 1.7). 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 different chemical environment to the interior and either exposed to vacuum or interacting with atoms of a matrix in which the 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 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. The inset in Figure 1.7 shows the measured strength of magnetism (or the *magnetic moment* per atom) for Co nanoparticles as a function of size. The data are described in more detail below.

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 5, Section 5.1.2) and pass them through a nonuniform magnetic field as shown in Figure 1.8. 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 Fe, Co, Ni, and Rh atoms within their bulk materials are $2.2\mu_B$, $1.7\mu_B$, $0.6\mu_B$,and $0\mu_B$ (Rh is a nonmagnetic metal), respectively. Figure 1.9 shows measurements of the magnetic moment per atom in nanoparticles

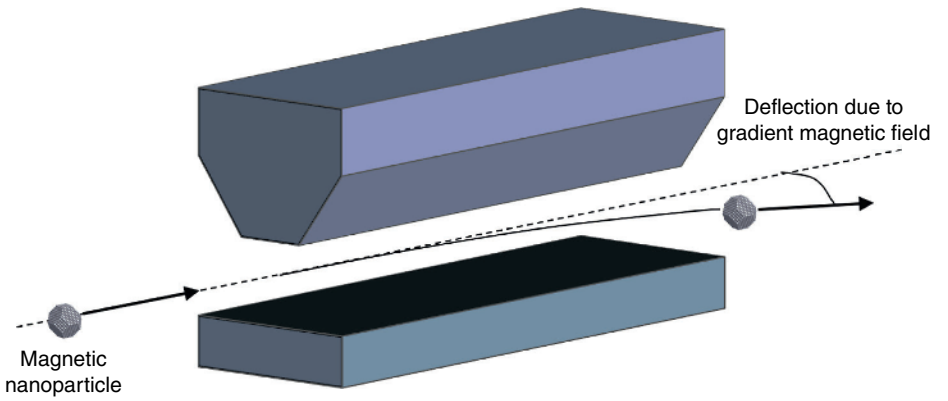

Figure 1.8 **Measuring the magnetic moment in free nanoparticles.** The magnetic moment in free nanoparticles can be measured by passing a beam of them through a nonuniform magnetic field and measuring the deflection in their path.

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

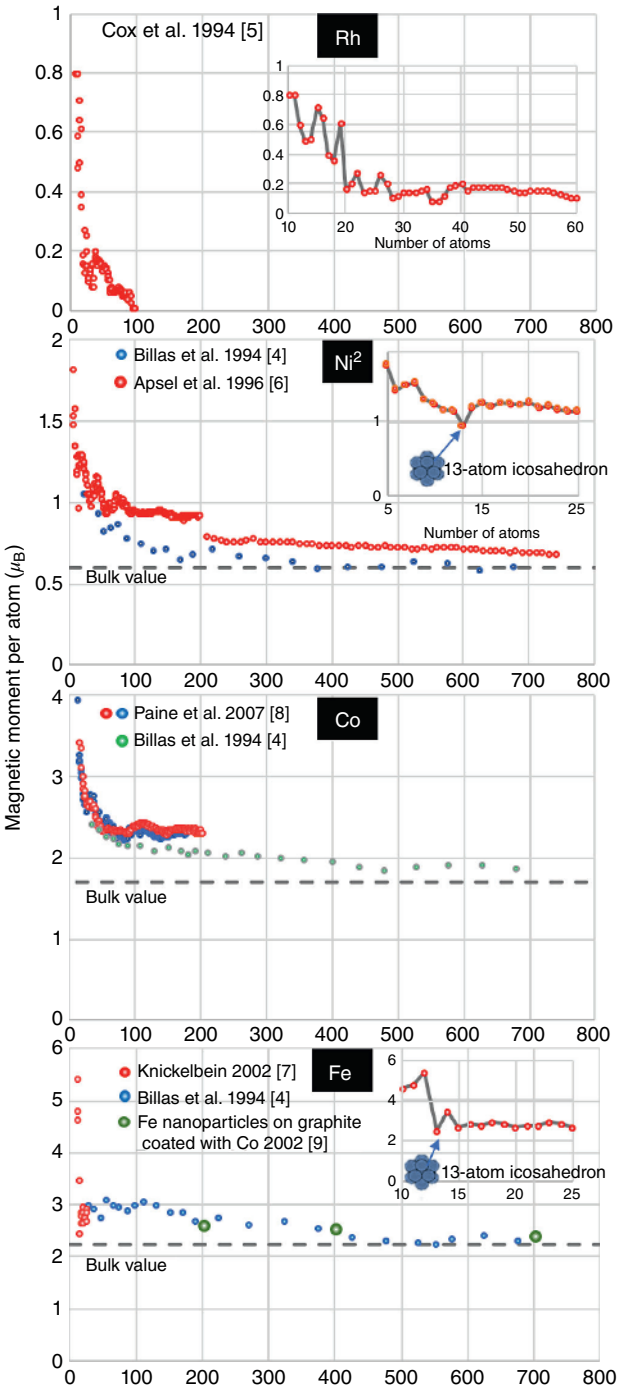

Figure 1.9 **Measured magnetic moments per atom in magnetic nanoparticles.** Experimental measurements of the magnetic moment per atom in Fe, Co, nickel (Ni), and rhodium (Rh – a nonmagnetic metal in the bulk) nanoparticles as a function of the number of atoms in the particle. For Fe, Co, and Ni, there is a significant increase in the magnetic moment per atom over the bulk value for particles containing less than about 600 atoms. Rh becomes magnetic in particles containing less than about 100 atoms. The insets show the sharp variations in magnetic moments at very small particle sizes. Note the very dramatic change in the magnetic moment of Fe particles in going from a 12-atom particle to a 13-atom particle (icosahedron). A similar dip in going from 12 to 13 atoms, though not so pronounced, is also observed in Ni nanoparticles. *Source:* Adapted from I. M. L. Billas et al. [4]; A. J. Cox et al. [5]; S. Apset et al. [6]; M. B. Knickelbein [7]; F. W. Paine et al. [8]. In the Fe curve are also shown measurements (green circles) for Fe nanoparticles supported on a graphite surface and coated with Co [9] (see text).

of the above four metals as a function of the number of atoms in the particle. In the case of Fe, Co, and Ni, 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 small particles (containing less than about 100 atoms) of the nonmagnetic metal Rh become magnetic.

Throughout the whole size range in Figure 1.9, 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. If Democritus was able to do his chopping experiment down to the nanoscale on Fe, 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 *a-tomon* as 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 magnetically dead to the full magnetic power of Fe with every atomic magnet aligned as the piece formed a single-domain particle. He would exclaim "I have reached the *a-tomon*, lets just try and cut again." Imagine his surprise, when he finds that the properties continue to change 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. Some of these changes can be dramatic, for example, if he was holding a 13-atom cluster 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 $6\mu_B$. The 13-atom piece is in a particularly stable configuration known as an icosahedron (20-sided solid), illustrated in the figure, and for reasons beyond the scope of this chapter, the high symmetry in this atomic structure reduces the magnetism. The same effect is seen in Ni, though less pronounced, in passing through the 13-atom size. The magnetism in very small Rh nanoparticles is particularly spiky showing peaks and troughs every two or three atoms.

So we can now see the reason why the nanoscale is special as a size, at least as far as materials are concerned. It represents the border region between the macroscopic world and the microscopic atomic world in which the properties of pieces of matter depend on size, and they display novel behavior only found in that size scale. 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. It is almost as if we could add a third dimension to the periodic table, so for each element, we can choose the size of the nanoparticle building blocks, which would modify the properties of the material produced. 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 Fe 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 Figure 1.10, which shows a thin film of Fe produced by depositing preformed nanoparticles onto a silicon substrate in vacuum. It is clearly a random stack of the deposited particles showing 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 from the nanoparticle stack.

As an instructive example of creating a high-performance material using nanotechnology, let's go through the steps necessary to produce a magnetic material with a higher magnetization than the best conventional alloy. The most magnetic practical metal available to the designers of machines and devices is Fe–Co alloy in an approximately equal mixture. This metal has an average atomic magnetic moment of $2.45\mu_B$ – about 10% higher than bulk Fe and has been

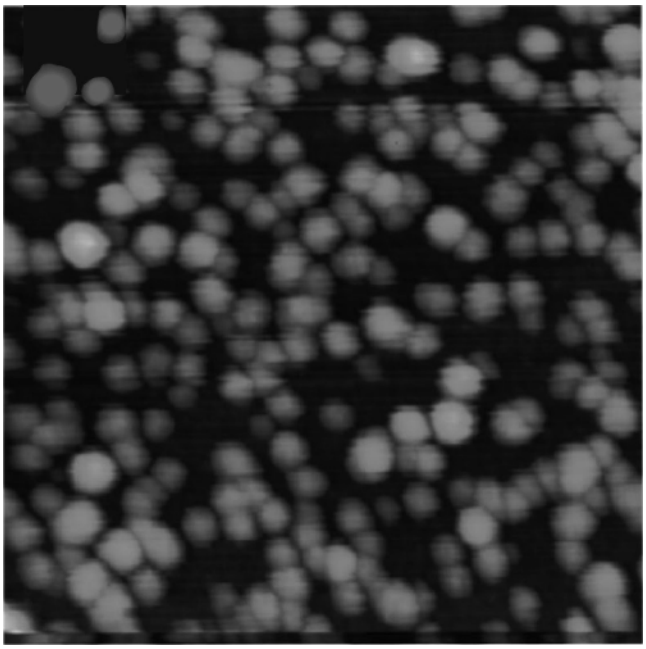

Figure 1.10 Morphology of nanoparticle film. STM image (see Chapter 5, Section 5.4.1) with an area of 100 nm × 100 nm of a thin film produced by depositing 3 nm diameter Fe nanoparticles onto a silicon substrate in vacuum. It is clearly a random stack of the deposited particles and the film properties will be different to those of a smooth film that would be formed by depositing Fe atoms. *Source:* Reproduced with the permission of the American Institute of Physics from M. D. Upward et al. [10].

known since 1912[4]. This magnetization known as the Slater–Pauling limit acts as a fundamental bound to the performance of a swathe of technologies ranging from electric motors to magnetic recording and despite a century of searching, no higher performance material has been found.

Yet, if we look at the data for Fe nanoparticles in Figure 1.9, the magnetization is higher than the Slater–Pauling limit for all sizes below about 300 atoms. This, however, is for isolated nanoparticles in a vacuum and it is not immediately clear how to make a material out of them while preserving the high value of the magnetic moment. About 20 years ago, the journey from isolated nanoparticles to materials started with experiments on size-selected Fe particles deposited in ultra high vacuum (UHV) onto graphite surfaces [9]. This work, showed that, for particles smaller than about 3 nm, the enhanced magnetic moments were retained when the particles were on a support and also revealed the source of the additional magnetic moment. Magnetism in atoms arises from two contributions, that is, the magnetic moment due to the orbital motion of the electrons, which can be considered as a tiny current loop, and from the electron "spin," which can only be understood from a quantum mechanical perspective. In a transition metal such as Fe, virtually all the magnetism is due to the spin with the orbital moment "quenched" almost to zero. In a nanoparticle, which has a very high proportion of surface atoms with a reduced co-ordination relative to the bulk, some of the orbital moment reappears and in addition, the spin moment is enhanced. The experiments mentioned above [9] showed that about half the enhancement of the magnetic moment in small particles comes from the spin moment and the other half from the orbital moment.

Although these measurements moved from free beam nanoparticles to those supported on a surface, they were still for isolated nanoparticles and did not show directly how to make a high moment material. Depositing an entire film of nanoparticles reduced the effect of the surface as the particles came into contact and both the orbital and spin moments converged with the bulk values. To make matters worse, films made by depositing preformed nanoparticles on a surface such as the one shown in Figure 1.10 are highly porous with an atomic density around 60% that of

4 The high magnetization was first observed in $Fe_{67}Co_{33}$ alloys, but the magnetically soft variant $Fe_{50}Co_{50}$ that is used commercially was patented in 1929 by G. W. Elmer.

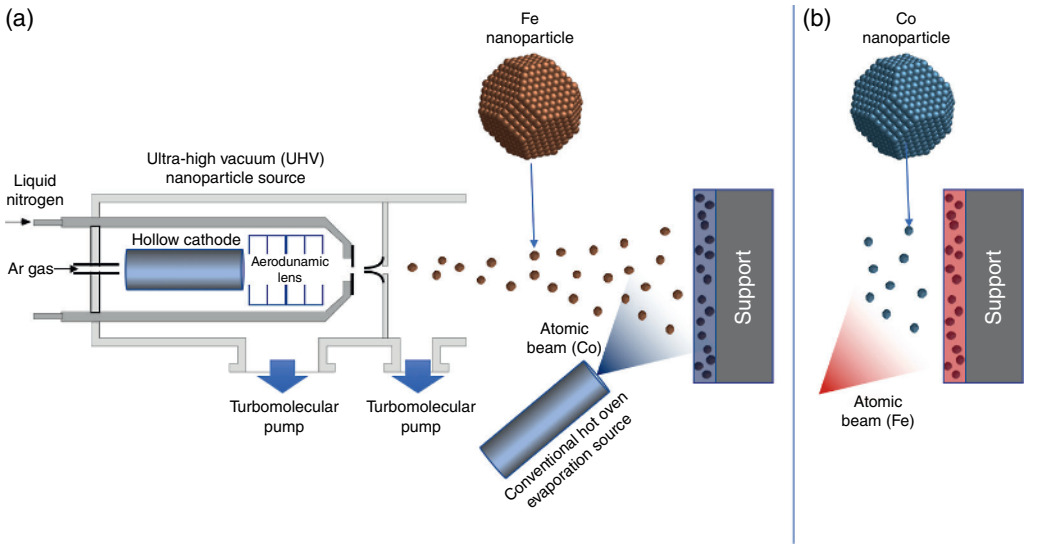

Figure 1.11 **Producing nanostructured films by cluster beam deposition.** Nanostructured films can be produced by depositing preformed nanoparticles from a UHV cluster source onto a substrate along with an atomic beam from a conventional hot oven evaporation source. (a) Fe nanoparticles in a Co matrix. (b) Co nanoparticles in an Fe matrix.

the bulk so the magnetic field produced by such a film would be less than that generated by bulk Fe. The same set of experiments, however, also showed that coating the Fe nanoparticles with Co while they were on the surface did not remove the enhanced orbital moment, and the Fe spin moment increased even further so that a total moment of $2.6\mu_B$/atom was recorded for 200-atom nanoparticles, compared to $2.2\mu_B$/atom in the bulk. The data from the Co-coated nanoparticles supported on a surface are plotted on the Fe nanoparticle curve in Figure 1.9 and it is observed that they show magnetic moments as high as the free nanoparticles but in a film that could be removed from its UHV environment without converting the Fe to oxide.

These experiments suggested a method to produce a thin film with a magnetization exceeding the Slater–Pauling limit, which is illustrated in Figure 1.11a. If Fe nanoparticles from a UHV nanoparticle source (see Chapter 5, Section 5.1.2) are deposited onto a surface in conjunction with an atomic beam from a conventional hot oven evaporator source, then an atomic film (matrix) containing embedded nanoparticles is created. The atoms fill all the gaps between the particles producing a film with the bulk density and each particle will retain its enhanced orbital and spin moments found in the aforementioned study. In addition, since the matrix has a very high proportion of interface atoms, it should display enhanced magnetic moments as well. Figure 1.11a shows Fe nanoparticles embedded in a Co matrix but clearly with this setup, it is straightforward to reverse the materials and produce films of Co nanoparticles in an Fe matrix as shown in Figure 1.11b.

A few years later this idea was confirmed and films with a magnetization exceeding the Slater–Pauling limit were produced [11]. The data are shown in Figure 1.12, which plots the magnetic moment per atom for Fe nanoparticles in Co matrices (red dots) and Co nanoparticles in Fe matrices (blue dots) compared to the Slater–Pauling curve for conventional Fe–Co alloys. Note that due to an accident of the units and the densities of Fe and Co, the conversion factor from

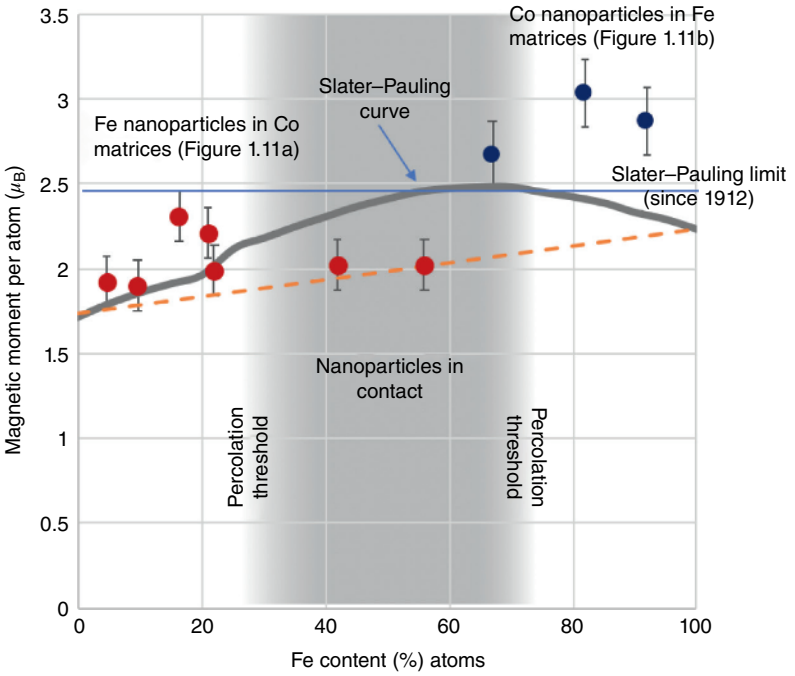

Figure 1.12 High-moment films produced by cluster beam deposition. Magnetic moment/atom in nanoparticle-assembled films compared to the Slater–Pauling curve.

magnetic moment per atom in Bohr magnetons (μ_B) to magnetic field produced in Tesla is very close to 1.0 so the two measures are often interchanged. The factors are 0.99 for Fe and 1.06 for Co so that the Co-rich end corresponds to a slightly higher magnetic field than the value indicated in μ_B/atom.

What the data clearly show is that the magnetization in the films of Fe nanoparticles embedded in Co matrices exceeds that of the Slater–Pauling curve till the density of nanoparticles reaches the percolation threshold at 25%. Then, the magnetization reduces to a value that is the weighted average of the Fe and Co bulk magnetic moments. This is due to the nanoparticles coming into contact and the Fe–Co interface reducing so that essentially there is a phase-separated mixture. It is evident from the data for the Co nanoparticles in an Fe matrix, however, that a saturation magnetization of about 3 T can be achieved, which is significantly higher than the Slater–Pauling limit. The data in Figure 1.12 are from a material rather than isolated nanoparticles, but it is still in the form of a very thin film approximately 50 nm thick, that is, a long way from a bulk material. With big improvements in the flux from nanoparticle sources, however, there are now patented ideas to produce bulk quantities of this nanostructured alloy, which the author's group is working on at the Universidad de Castilla-La Mancha in Spain. It is envisaged that this material will find its way into motors for all-electric transport within eight years where it will produce at least a 20% improvement in the power to weight ratio of the motor.

This development has been labored as it is an excellent example of incremental nanotechnology moving from the lab into applications. This is just a single example and the method of producing materials shown in Figure 1.11 is a supreme way of making nanostructured materials in general.

One can control the grain size independently of the volume fraction, there is free choice of the material in the grains or the matrix, and it is possible, using methods shown in Chapter 5, to make the nanoparticles out of more than one material in a range of motifs. These include alloy, core-shell, and dumbbell nanoparticles, also called Janus particles as they have two different materials exposed at the surface. The method is likely to find its way into a range of applications in advanced materials.

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 hardness, which is given by the amount another body such as a ball bearing or diamond is able to penetrate a material, and 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 Figure 1.13a, 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, etc. It is possible by various techniques including nanoparticle deposition (Figure 1.11), electro-deposition, and special low-temperature milling methods to produce metal samples in which the grains are a few nanometers across. An example is shown in Figure 1.13b, where, on the same scale as Figure 1.13a, the grain structure disappears to show a homogenous material. Blowing up the magnification a further 15 000×, however, (Figure 1.13c) 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 highlighted for one of the grains. Whereas in the coarse-grained metal shown in Figure 1.13a, 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.

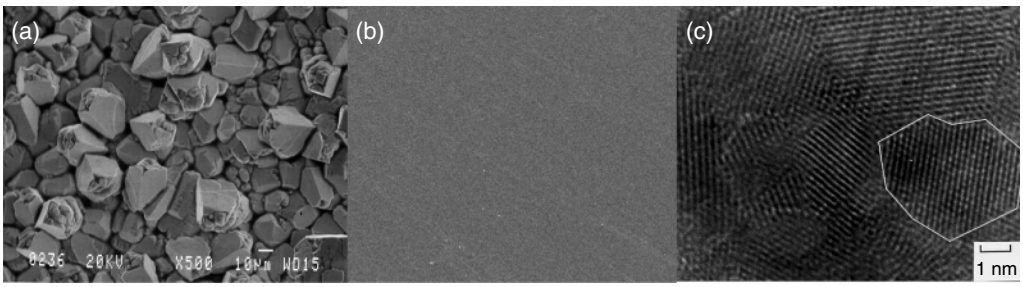

Figure 1.13 **Grain size in nanostructured materials.** Electron microscope images showing a comparison of the grain structure in conventional and nanostructured materials. (a) Conventionally processed material (tin) showing a typical grain size of about 20 μm. (b) Nanovate™ nanostructured Ni-based coating 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. *Source:* Reproduced with permission from Integran Technologies Inc. (http://www.integran.com).

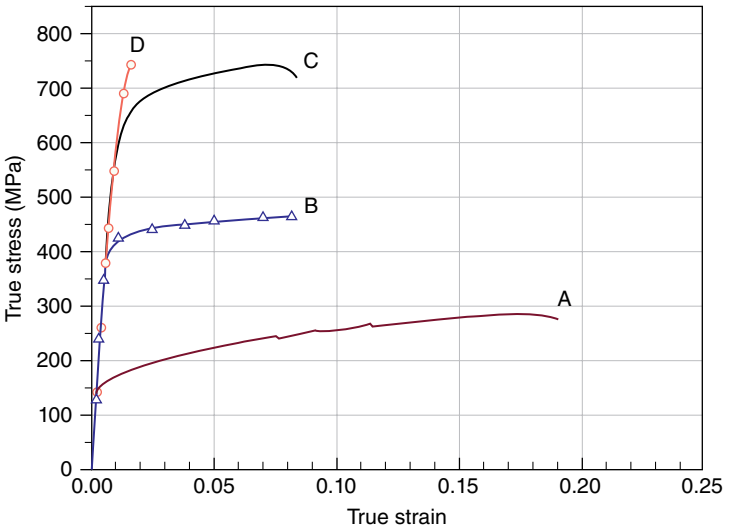

Figure 1.14 **Yield strength of aluminum alloys.** Comparison of Deformation (Strain) vs. Load (Stress) for aluminum alloys with different grain sizes. A is a normal aluminum alloy (coarse-grained). B – D Nanostructured aluminum alloy containing grains of size ~30 nm produced by various processes. The plastic limit occurs at the point where the slope changes and the nanostructured materials have a value that is up to four times higher than the conventional alloy. *Source:* Reproduced with the permission of Elsevier Science from K. M. Youssef et al. [14].

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 control the grain size right down to the nanometer scale can produce significant 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 1.14 shows a plot of the strain (relative elongation of a sample) vs. stress (load) for various nanostructured aluminum alloys compared to normal (coarse-grained) aluminum alloy [14]. 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 than 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 plot, however, and that is that 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 it is so highly valued since it does not corrode or tarnish and so 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). Gold would therefore

seem to be useless as a catalyst to speed up chemical reactions, but this is not so for gold nanoparticles. Catalysts provide a surface whose chemical properties reduce the energy required for a specific reaction between two other species to occur and are vital to the chemical industry. Because it is only the surface that is active, catalysts are in the form of nanoparticles to maximize the surface area per gram of material (see Problem 1) and so their chemical properties are different from the bulk form, which is also true for 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.

An 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 1.15 shows a compilation of data on the oxidation of carbon monoxide (CO) by 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 co-ordinated atoms are where the reacting carbon monoxide (CO) molecules preferentially bond during the reaction. The fraction of this type of atom (highlighted in red in Figure 1.15) is proportional to $1/d^3$, where d is the particle diameter, and the black line in Figure 1.15 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 a 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 significant research activity.

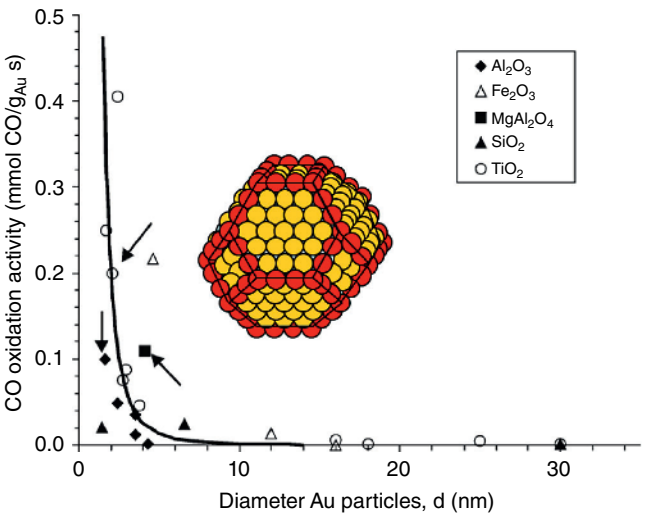

Figure 1.15 **Reactivity of gold nanoparticles.** Measured activities of gold nanoparticles on various supports (box) for carbon monoxide oxidation as a function of particle size. The black line is a fit using a $1/d^3$ law and is seen to broadly represent the variation indicating that the dominant size 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. *Source:* Reproduced with the permission of Elsevier Science from N. Lopez et al. [16].

1.5 Nanoparticles Interacting with Bacteria and Viruses

Chapter 8 deals in detail with nanoparticles interacting with living systems, and the introduction described types of nanoparticles that could be used for treating cancer (see Figure I.5). In this section, just one type of application will be considered where size is important and that is nanoparticles, mostly silver, interacting with bacteria and viruses, which has become an increasingly important area for medical research. 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 as new antibiotic-resistant strains have become a serious problem in public health. For example, in 2017, such bacteria killed more than 35 000 people in the United States alone [17] and any method of attacking them, not involving normal antibiotics, is becoming increasingly important.

Before the discovery of antibiotics, silver was used as an antiseptic in the treatment of open wounds and burns. The highly reactive silver ions can bind to the bacterial cell walls inhibiting the cell respiration or they can pass into the cell and denature the bacterial DNA, which inhibits the replications and ultimately leads to cell distortion and death. Silver in the form of chemical compounds applied to wound dressings, although effective, was shown to be less effective than conventional antibiotics [18].

Silver has made a comeback in the form of nanoparticles, however, because of its greatly increased effectiveness, 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, entire nanoparticles are sufficiently small to pass through outer cell membranes and enter cells' inner mechanisms. A study using nanoparticles with a wide size range [19] showed that only silver nanoparticles with sizes in the range 1–10 nm were able to enter cells and disrupt them. 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 1.16 shows an electron microscope image of some *Pseudomonas aeruginosa*[5] 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 as 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. Other metal nanoparticles such as copper, magnesium, titanium, gold, and zinc have also been found to be effective antibacterial agents and one attractive aspect of using inorganic materials such as these is that it is harder for bacterial cells to evolve ways to become resistant.

There has been less research on the antiviral effectiveness of nanoparticles but it has become a more active topic of research following the Covid-19 pandemic of 2020. Viruses are much smaller than bacteria and are inhabitants of the Nanoworld as illustrated in the introduction (see Figure I.1). The original report of the interaction of silver nanoparticles with viruses came in 2005 from the same team that carried out the work described above on bacteria [20]. They exposed HIV-1, the virus responsible for AIDS, to silver nanoparticles and discovered that, again, the important size range is 1–10 nm. As shown in Figure 1.17c, nanoparticles of this size attach themselves in an ordered array on the surface of the virus. The HIV-1 virus is covered in a regular arrangement of glycoprotein "knobs" (Figure 1.17a), and the average distance between the silver nanoparticles in the image suggests that they attach

5 Bacterium that infects the lungs of cystic fibrosis sufferers and causes inflammation and breathing problems.

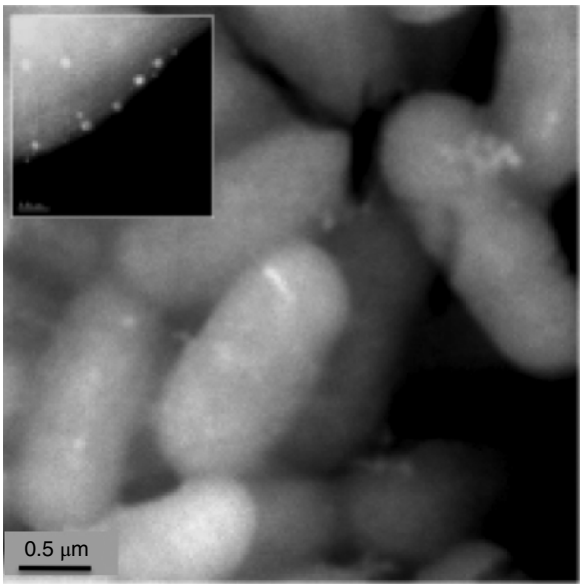

Figure 1.16 Silver nanoparticles attacking bacteria. Electron microscope image of *P. aeruginosa*[5] bacteria after exposure to silver nanoparticles. The particles with size ranges 1–10 nm are active in disrupting the cell function. The inset shows a high-resolution image of some particles attached to the cell's outer membrane. *Source:* Reproduced with the permission of the Institute of Physics from J. R. Morones et al. [19].

themselves to these knobs. The team went on to demonstrate that the nanoparticles prevent the virus from binding to host cells. Viruses on their own are not able to replicate, so they need to enter the cells of the host and ambush the biological machinery of the cell to make copies of themselves. They anchor onto cells via the glycoproteins to gain entry via the cell membrane, so attaching nanoparticles onto the proteins as in Figure 1.17c prevents the virus particles from entering the host cells and they are left floating around homeless till they get picked up by the immune system.

Since the original work, silver nanoparticles have demonstrated strong antiviral potential against several other viruses, including herpes simplex, hepatitis A virus, hepatitis B virus, huma papillomavirus, and respiratory syncytial virus [21, 22]. All of these viruses have a similar general morphology to that shown Figure 1.17a with a roughly spherical shape and a diameter in the range 40–200 nm, that is straddling the boundary of the nanoworld. They all have an array of glycoproteins on the surface and it is thought that the silver nanoparticles act against them in the same way as in the case of HIV, that is, binding to the glycoproteins and locking the virus out of the host cells. As in the case of bacteria, it is harder for viruses to become resistant to silver nanoparticles as compared to conventional antiviral agents

Here, we have only encountered very brief sketches of a couple of examples of applications of nanoparticles in healthcare. This is a huge and burgeoning field and a more comprehensive discussion is postponed until Chapter 8. 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. This can either mean 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 from 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

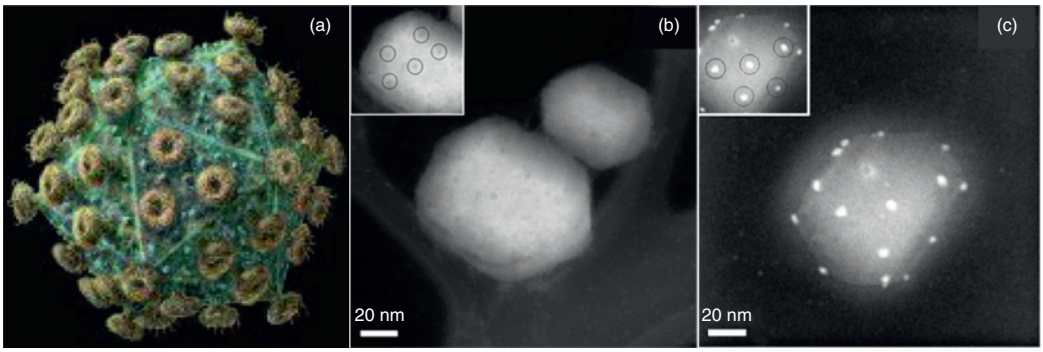

Figure 1.17 Silver nanoparticles attached to HIV-1. (a) Computer-generated image of HIV, showing glycoprotein "knobs." *Source:* Reproduced with permission from www.virology.net/Big_Virology/BVretro.html. (b) Electron microscope image, with inset superimposing position of glycoprotein knobs. (c) Electron microscope image of virus after attachment of silver nanoparticles. *Source*: Reproduced with the permission of BioMed Central from J. L. Elechiguerra et al. [20].

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 as diverse as magnetic recording to medicine. All the types of nanoparticles 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 averages at 10^{-5} eV/atom. Use the data to estimate the maximum size of a spherical single-domain particle. (Hint: assume the exchange interaction only operates between atomic neighbors, whereas in a small particle the dipolar interaction affects all atoms equally. In addition, for an estimate, assume the atoms are cubes with a width of 0.2 nm).[6]

6 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[a] 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.

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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