

# Nanosciences and Nanotechnology

**Evolution or Revolution?** 





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Jean-Michel Lourtioz · Marcel Lahmani Claire Dupas-Haeberlin · Patrice Hesto Editors

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#### **Foreword to the French Edition**

Nanotechnology can produce objects with hitherto unimagined architectures and it is unique, not only for its spinoffs in every area of science and technology, but also for its economic and social consequences.

It is interesting to observe that specialists have some difficulty agreeing on a precise definition of nanoscience and nanotechnology. Physicists, chemists, and biologists often refer to different size ranges, but they all agree that the nanoworld is characterised by a radical change in the physical, chemical, or biological properties of the objects in question. Indeed, nanotechnological development is not just the business of miniaturising matter. It can be used to produce novel and often unexpected features, such as the appearance of remarkable optical properties, the creation of molecular motors, and the possibility of navigating within human cells. It should thus come as no surprise that nanoscience and nanotechnology find many often cross-disciplinary applications in areas as varied as electronics and information systems, energy, optics, materials, and nanomedicine. So nanoscience is neither physics, nor chemistry, nor biology, but all these disciplines at the same time, as they converge toward the nano scale. Furthermore, in the nanoworld, simple ethical and philosophical questions can sometimes be difficult to answer. For example, a protein can be synthesised by a nanomachine consisting of an mRNA associated with a ribosome. On this scale, are we already dealing with the living or can we treat this using a mechanistic description of elementary molecules?

It would be hard to say at the present time whether the 'nano' field will simply continue as it is today, whether it will gradually fade from view, or whether it will tend toward different concepts and applications. Breakthrough technologies are unpredictable by their very definition. But I am quite convinced that international competition will be determined by a country's ability to promote cross-disciplinary interactions in the truest sense of the term, of the kind that occur in the cafeteria when research staff and students of different fields are housed on the same site and can exchange ideas about new concepts and methods. It is sad to say that such points of exchange and interdisciplinarity have not yet been put to the fore in France.

The main goal of this book is thus to present an integrated and cross-disciplinary description of nanoscience and nanotechnology. It aims at a very broad readership from undergraduates to researchers who would like to obtain a clear overview of the ideas and applications of nanoscience and nanotechnology in an area where they may not have specialist knowledge. But since all studies of future prospects suggest that nanotechnology will lead to economic development and the creation of wealth, the book also takes into account the executives and decision-makers across a range of industrial sectors. In fact, the different chapters can be read independently, while the deliberately selective bibliographies focus on the main advances in the given field and can be used as a starting point for further investigation.

The very general introduction to the book deals with the nanometric scale, describing the nanoworld and its applications in the fields of nanomaterials, nanoelectronics, and health. The basic principles involved in making nano-objects are also discussed, viz., the bottom—up and top—down approaches. The remainder of the book is divided into four parts.

The first of these takes a detailed look at nanophysics, nanoelectronics, and nanophotonics. It shows that quantum effects and surface phenomena play a crucial role in the nanoworld and lead to remarkable properties. Boxed explanations provide a comprehensible overview of the physical principles underlying the radically different properties observed in the nanoworld, describing among other things the tunnel effect, which makes short work of potential barriers on the nanoscale, and the notions of spin and magnetic domains. The author of Chap. 2 also discusses the way nanophysics may develop tomorrow in his opinion, with ever greater involvement of quantum effects. It remains an open question whether it will evolve into picophysics, i.e., physics on the picometric scale, which corresponds to the world of individual atoms, manipulating them tomorrow as we build up structures today from individual molecules.

The second part focuses on the ways nanochemistry can contribute to the discovery and design of new (nano)materials. As the author of Chap. 5 so clearly explains, chemistry is already a nanoscience, since it manipulates and synthesises nanometric entities, from atoms to molecules, polymers, and colloids with varying degrees of complexity. Novel carbon-based nanomaterials such as fullerenes, graphene, carbon nanotubes, and nanodiamonds are also discussed. A large part of the chapter is devoted to the role of molecular and supramolecular chemistry in the field of nanomaterials, as exemplified by the so-called click chemistry', which aims to functionalise nano-objects or self-assemblies resulting from interactions between molecular entities.

The third part devoted to nanobiotechnology concentrates mainly on nanomedicine. This discipline has become a field of investigation in its own right, as attested by the attribution of a chair at the *Collège de France* in 2009–2010. As explained in the ensuing chapters, the application of nanotechnology to medicine includes therapy through targeted drug delivery, in vitro and in vivo medical diagnostics, and combinations of the two (theranostics), but also regenerative medicine for the reconstruction of organs and tissues. All these areas are discussed, as are the consequent ethical and regulatory questions. The preclinical development

of a nanomedicine is also illustrated by a concrete example, namely the use of squalenisation to design anti-cancer and anti-infective nanodrugs. Apart from nanomedicine, two further chapters deal with matters of toxicology. One treats the impact of nanotechnology on human health, and the other environmental risks.

The last part, entitled *Nanotechnology and Society*, provides a detailed overview of industrial and research institutions currently engaged in this field, both in France and in the rest of the world. It also describes the various courses available in France and across Europe, and shows how the cross-disciplinary nature of nanoscience and nanotechnology makes it possible to teach science at every level of education without necessarily having to make sacrifices to the fundamentals of the traditional disciplines. The field of nanotechnology is undoubtedly a subject of tough industrial competition in the worldwide pursuit of patents and funding. As demonstrated in the last chapter of this part, such intense competition requires strict international regulation, taking into account the potential risks inherent in nanotechnology.

The present work illustrates the wealth and diversity of knowledge generated by nanoscience and nanotechnology, and it will help readers to form their own opinion in answer to the question raised by the underlying theme of this book: will nanoscience and nanotechnology turn out to be an evolution or a revolution?

July 2013

Patrick Couvreur Université Paris-Sud and Institut Universitaire de France Chatenay-Malabry

#### **Preface to the French Edition**

The series of books on the nanosciences originally instigated by Marcel Lahmani and Philippe Houdy already comprises four multi-author books with a largely didactic objective, each tackling one of the main scientific disciplines, and aimed at readers who have already reached graduate level. The first volume, entitled *Nanotechnologies et nanophysique*, was published in 2004 and reedited twice in 2006 and 2009. This was followed in 2006 by a second volume, entitled *Nanomatériaux et nanochimie*, reedited in 2012. Then came *Nanobiotechnologies et nanobiologie* in 2007 and *Nanotoxicologie et nanoéthique* in 2010. <sup>1</sup>

The original French versions of the series were nominated four times for the Roberval Prize and the series as a whole was awarded the *Trophée Roberval*, the highest award attributed by this institution. Naturally, all the credit must go to the researchers and engineers who wrote the contributions, along with Belin for the French publication and Springer for the English version, but not forgetting perhaps the stubborn determination of those who initiated the project.

The present work differs significantly from its predecessors. Indeed, the main motivation here is to give a didactic overview of the key areas of science that relate in some way to nanotechnology, and this for a broad non-specialist public. The book thus stands out by the diversity of themes covered, each illustrated by a broad range of examples, leading to numerous applications of immediate interest to the world of industry. It refers to all the scientific disciplines whose development is in some way affected by nanoscientific endeavour, from physics in the form of electronics and photonics, through chemistry and materials science to biology and medicine, not forgetting the inherent toxicological issues. In the last part of the book, there is a guide to, or rather an inventory of, all the current actors on the French scene, including research institutes, educational establishments, and industrial sites. This is intended to provide students, researchers, and engineers with

<sup>&</sup>lt;sup>1</sup>Concerning the English edition, the first volume, entitled *Nanotechnologies and Nanophysics*, published in 2007, was followed by a second, entitled *Nanomaterials and Nanochemistry*, the same year. Then came *Nanobiotechnology and Nanobiology* in 2010 and *Nanotoxicology and Nanoethics* in 2011.

a clearer picture of all the nano activities going on in our country. The book ends with a review of possible social implications of nanotechnology and current regulation. A glossary of some 200 terms has been compiled to provide the reader with the terminology needed to get a good grasp of the subject matter in each chapter.

The second aim was to update the themes in each of the disciplines covered in the previous volumes and thereby bring out the cross-disciplinary nature of nanoscience and nanotechnology and the high level of interaction they generate between research and industrial applications. Particular stress has been put on recent progress in research at the interfaces between physics and chemistry, physics and biology, chemistry and medicine, and between physics and chemistry and the life sciences.

To illustrate the links between research and industry, we have included with the main chapters short articles describing the prospects for nanotechnology in industrial sectors which will in certain cases come as something of a surprise to the general public.

And last but not least, our third aim has been to answer the following question: will nanoscience and nanotechnology lead to a scientific and industrial revolution, as was announced some fifteen years ago?

The reader will soon realise the enormous amount of research that has been carried out in recent years, and will no doubt understand the need to pursue this exploration of the nanoworld for some time to come, knowing that chance will surely surprise us with further extraordinary discoveries as only she knows how!

#### Acknowledgements

First and foremost, we thank all the authors of the different chapters for their commitment to this undertaking and the quality of their contributions. The choice of authors was made with a view to updating the topics discussed in the previous volumes of the series, including the latest work by several researchers, teachers, and professionals responsible for presenting recent nanotechnological applications. There is also an exhaustive inventory of the relevant resources available in France, together with the latest regulations currently in force.

The main task of the editorial committee has been to dialogue with the authors and edit the resulting manuscripts with an eye for didactic content and the aim of producing a coherent whole. The entire project was supervised by Jean-Michel Lourtioz.

We would particularly like to thank Jean Dutour for the many illustrations, Jean-François Pône for his invaluable assistance at various stages in the preparation of the book, Stephen N. Lyle for his excellent translation of the French edition, EMRS and Springer for their financial suppport to the English edition and Cécile Foullon, who provided the interface with the publisher Belin, for the huge task of formatting and finalising the submitted texts to make them accessible to as broad a readership as possible.

We also extend our warmest thanks to Patrick Couvreur who kindly accepted to write the foreword to our book.

This project was backed both morally and financially by UniverSud Paris and Labex NanoSaclay, to whom we express our gratitude. From 2007 to 2014, the association UniverSud Paris has brought together three universities and three *Grandes Ecoles*, and in 2015 it has been incorporated into a still larger association, of international importance, the University of Paris-Saclay. The Labex NanoSaclay will house all the nano research teams of this future university.

September 2013

Jean-Michel Lourtioz Marcel Lahmani Claire Dupas-Haeberlin Patrice Hesto

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## Chapter 1 Introduction

Louis Laurent

**Abstract** During the twentieth century, progress in physics, chemistry, and biology brought a detailed understanding of the structure and properties of both living and inert matter on the nanometric scale, i.e., lengths of the order of one billionth of a metre. By the end of the 1950s, instruments were being developed to observe, manipulate, and assemble matter and devices on this same length scale. It was thus clear that the convergence of all this knowledge would open the way to spectacular applications, and yet it was not until the 1990s that nanotechnology truly came into its own. The most visible application was without doubt nanoelectronics, today present in an increasing number of products which are in the process of changing our lives. But nanotechnology is being put to work in many other sectors such as materials, sensors, energy, and medical applications. Thousands of products contain nanosized ingredients and, given the scope of these developments, concern has been expressed, particularly about the possible toxicity of nanoparticles and inadequate control of industrial applications. Since its inception, nanotechnology has been closely associated with the notion of economic growth, but its maturity will also depend on an understanding of the associated risks and its contribution to the crucial future questions of sustainable development.

#### 1.1 There's Plenty of Room at the Bottom

Nanoscience and nanotechnology get their definition primarily from a scale of length, viz., the nanometer, which is a billionth of a meter. To see what this means, consider a hair. This will grow about a centimeter every month. Carrying out a simple calculation, we discover that this hair will grow at a rate of about four nm per second. But why does the nanometer play such an important role? To answer this, we must turn to the very constituents of matter.

The matter around us is made up either of atoms, which can be represented as tiny spheres with diameters of the order of a few tenths of a nanometer, or of molecules,

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which are strongly bound assemblies of atoms measuring a few nanometers across. In other words, the smallest amount of a substance we can speak about does indeed concern this length scale. Atoms are so small that, in our everyday lives, we are unlikely ever to feel as though we are made up of such things. Even what we consider to be microscopic comprises a huge number of atoms. For example, a bacterium in the form of a rod 3000 nm long contains a hundred billion atoms, enough to build up the complex machinery that allows this bacterium to live. Simpler than the bacteria, viruses measure a hundred or so nanometers and still contain tens of millions of atoms. Likewise, sometimes highly complex microscopic systems can be made by industry, such as microprocessors, with features now measuring only a few tens of nanometers. This was the 'nanoworld' that Richard Feynman, Nobel Prize for Physics, was referring to in the title of a talk he gave on nanoscience back in 1959: *There's plenty of room at the bottom*.

#### 1.2 A Short History

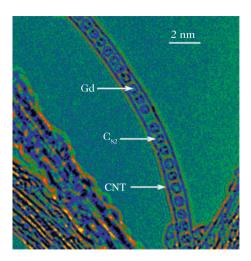
The idea that the world is made of atoms is not a recent one. It is attributed to the Greek philosopher Leucippus and his disciple Democritus (circa 400 BC). However, it was not until the nineteenth century that progress in the sciences turned this into a serious hypothesis and then a reality, with implicit reference to the nanometric length scale. Between the end of the nineteenth century and the middle of the twentieth, techniques were developed for observing matter on this scale. For example, in 1931, two German engineers Ernst Ruska and Max Knoll invented the electron microscope. The underlying idea can be understood by comparison with the optical microscope, except that light is replaced by electrons which probe matter in much finer detail. After ten years or so, the electron microscope could already achieve a resolution of 10 nm, and further progress was made right through the twentieth century. A resolution of 0.1 nm, the size of a single atom, was reached in the 1990s. Figure 1.1 shows an example of such an image.

It was also in the 1980s that techniques were improved for laboratory manipulation of matter on the nanometric scale. A symbolic step was the invention of the scanning tunnelling microscope (STM) by two researchers at the IBM research center in Zurich, Heinrich Rohrer and Gerd Binnig. If the electron microscope is likened to a kind of ultra-powerful eye, the scanning tunnelling microscope could be described as a sort of finger that investigates matter by prodding it. A fine tip is displaced across the surface of the matter, so delicately that it can 'feel' the very atoms themselves on the surface. In the original version, invented in 1981, this sensing was carried out using electricity. As we shall see later on, each atom on the surface 'attracts' electricity. Then, from 1986, another version of the microscope appeared, measuring

<sup>&</sup>lt;sup>1</sup>However, it should not be thought that there is nothing smaller than an atom. The atom is itself a complex object, made up of elementary particles much smaller than the nanometer, but this matter is no longer of the kind we see around us.

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Fig. 1.1 Bright-field electron microscope image of Russian nanodolls showing tube-shaped structures made of carbon atoms, known as carbon nanotubes (CNT). Inside these nanotubes are small spheres called fullerenes, each made from 82 carbon atoms (C<sub>82</sub>). Each fullerene itself encloses a gadolinium (Gd) atom. Courtesy of A. Gloter, Solid State Physics, Orsay, CNRS France-AIST Japan



the attraction exerted by each atom on the tip. This was the atomic force microscope (AFM). These much cheaper devices soon became commonplace in research establishments. Even more spectacularly, the tip of an atomic force microscope can actually displace a single atom. A symbolic event here was the feat achieved by Don Eigler who, in 1989, deposited 35 xenon atoms on a nickel surface to write the IBM logo. (Don Eigler worked for IBM.) This symbolic image is easily found on the Internet even today.

In parallel with these technical achievements came a growing understanding of the behaviour of matter on the microscopic scale. A good example is provided by the science of colloids. These are tiny pieces of matter with nanometric dimensions suspended in air or water. They are present throughout nature, e.g., milk is a colloid suspension. They were first identified in the nineteenth century, and were observed at the beginning of the twentieth century using the ultramicroscope invented by the chemist Richard Zsigmondy. However, it was only later in the twentieth century that colloid science came into its own, with industrial applications to materials, foods, cosmetics, and pharmaceuticals.

Another example is provided by molecular biology, which seeks to explain the way living organisms operate through the interactions between molecules taking place in cells. This science appeared in the 1930s, and over the next fifty years or so gave rise to a completely new outlook on cell dynamics and the advent of biotechnology.

A last example, but no doubt the most spectacular of all, is the development of microelectronics. The extraordinary expansion in this field at the end of the twentieth century brought the pursuit of ever smaller devices into the limelight. The first integrated circuit was invented in 1958 by Jack Kilby of Texas Instruments. This device integrates several components including transistors on a wafer of semiconducting materials and is ideally disposed to miniaturisation, provided that one has machines capable of making and positioning tiny components with sufficient accuracy.

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As time went by, these different areas of understanding came together to form a field in its own right, the field of nanoscience (or nanotechnology when we speak of applications), taking up Richard Feynman's far-sighted challenge. The main lines of research were many and varied and the applications even more diverse. The unifying feature came above all from the length scale at which the different phenomena were taking place. The word 'nanotechnology' itself is attributed to professor Norio Taniguchi of Tokyo university who, in 1974, used this term to describe techniques for fabricating semiconductors. However, it was not until the end of the 1990s that the new field reached maturity. Various nanotechnological instruments, including the famous scanning tunnelling microscope, were by then available commercially and becoming standard equipment in research centers. At the same time, the microelectronics industry was well on the way down the road to miniaturisation and had already reached the scale of 200 nm, with the symbolic landmark of 100 nm in view. The prefix 'nano' was becoming common currency in the world of research and governments the world over were launching their first nanoscience and nanotechnology programmes, the former when concerned with improving understanding and the latter when they had applications in mind.

#### 1.3 The Nanoworld

So what caused this sudden interest? The point is that, largely because it is being observed at these very small length scales, matter has very different properties, and while many of these properties can be deduced from laws of physics that have been around for over a century, it is only recently that observation and fabrication techniques have actually been able to demonstrate their existence, let alone build devices that put them to use.

#### 1.3.1 Matter on the Scale of a Few Atoms

Researchers routinely manipulate small clusters of atoms, deposit ultrathin layers, and shape devices to an accuracy of 10 nm. The granular nature of matter on the atomic scale then becomes fully manifest. Solids and liquids look like more or less regular assemblies of atoms or molecules which hold onto one another via forces ensuring overall cohesion. The atoms will sit a few tenths of a nanometer apart. A cube of side 10 nm will contain roughly 25,000 atoms, although the exact number will depend on the material. Another important point is this: the smaller the objects, the greater the proportion of atoms that will lie close to the boundary of the nano-object. For example, 20% of the atoms in the above 10 nm cube will be located at its surface. If we ourselves were microscopic and observed the world, two properties in particular would look strange.

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The first of these is thermal agitation. On this scale, each atom, molecule, or cluster will be in permanent vibratory motion. When Scottish botanist Robert Brown observed this motion in pollen grains in 1827, it gave him the impression that the grains were alive. In a solid, an atom will often simply oscillate vigorously, otherwise held in place by its neighbour, although it may sometimes pass between them. In a liquid, it will move around and regularly change neighbours. But in a gas, it will hurtle headlong like a cannonball until it comes up against another atom or the wall of the container. And the hotter the matter, the more agitated the atoms become. At room temperature, this agitation corresponds to speeds of a few hundred meters a second. Sometimes we must cool an object under investigation in order to reduce this agitation.

Another disconcerting phenomenon is cohesion. Two small fragments of matter, whatever kind of matter it may be, will strongly attract one another like two magnets. These forces are basically of electrical origin. Atoms are made up of a positively charged nucleus surrounded by negatively charged electrons in such a way that the object as a whole is electrically neutral. However, these charges reorganise themselves all the time, and a (sophisticated) calculation reveals that the attraction between opposite charges wins through. This phenomenon is often exploited by researchers to build nano-objects. When separate components, molecules, or atoms are brought together, they will stick to one another, often forming very regular patterns. This force has a range of only a few nanometers and so would be quite imperceptible on the scale of our own world. But it is this force that ensures that solids maintain their cohesion or that water forms droplets, unless they are heated up so much that the atoms are agitated enough to escape completely.

#### Forces

Let us take a closer look at the forces exerted between two objects in the nanoworld. On this scale, it is more convenient to use the nanonewton as unit of force. This is one billionth of a newton. This force is roughly equal to the weight of a sphere of radius 3 hundredths of a millimeter filled with water and containing 3.4 million billion water molecules.

Strong Bonds When two atoms join up in a chemical reaction by sharing their electrons, remaining firmly and permanently attached to one another at a separation of only a fraction of a nanometer, we say that they form a covalent bond. On the scale of the nanoworld, the force in a covalent bond is truly colossal. Indeed, to separate the two atoms forming a hydrogen molecule, one must exert a traction force of the order of a nanonewton, i.e., as we have seen, equal to the weight of a million billion hydrogen atoms. Such a force is hard to imagine on our own scale. If the two hydrogen atoms corresponded to two peas each weighing one gram, the force between them would be equal to the weight of 100 million Airbus 380 aircraft. This explains why hydrogen and many other molecules are so stable, making it very difficult to remove their atoms.

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Weak Bonds When they are placed a distance of the order of a nanometer apart, i.e., several atomic diameters, atoms and molecules do not join together. When they come close enough, however, they attract under the influence of electric force, any gravitational attraction being completely negligible in comparison. These forces, known as van der Waals<sup>2</sup> forces, are of the order of a thousandth of a nanonewton, which is a hundred to thousand times weaker than covalent binding forces. They are nevertheless very strong. If the atoms were two peas placed a centimeter apart, they would attract with a force corresponding to 100,000 Airbus 380 aircraft. This is why, on the length scale of the nanoworld, everything is 'sticky'. However, there is another phenomenon that prevents matter from clumping together, and this is thermal agitation. When it gets hot enough, atoms that are stuck together begin to dissociate due to repeated impacts from neighbouring atoms. Room temperature often suffices for this dissociation. In other case, more heat must be supplied.

**Sticky Nano-Objects** Attractive forces play a major role in the dynamics of nano-objects. To begin with, they ensure cohesion, unless it gets too hot. However, they also cause nano-objects to stick easily to anything passing within their range. So when a cluster of carbon atoms of radius about 50 nm, which will contain around 60 million atoms, comes close to a container wall, each atom in the cluster will be attracted to that wall. It will thus stick to it, attracted by a force of several nanonewtons, i.e., 200 million times its own weight.

#### 1.3.2 Electricity

When electrons move through matter, we observe an electric current on our scale. The 10 A that trigger a circuit breaker correspond to 60 billion billion electrons going by every second. Although each electron is not really a little grain of electricity carrying its charge, this is a convenient way on our scale to describe the current passing through a metal.

We have been making nanoscale electrical devices for several years now. The basic building blocks can be nanocavities a few nanometers across which store electrons, nanowires which carry a current, or films a few atoms in thickness. Some of these devices are found only in the laboratory, while others are mass-produced by the microelectronics industry. There is also the prospect of 'ultimate' electronic devices in which electrons are manipulated one by one. On the nanoscale, quantum mechanics becomes an essential tool for describing the behaviour of the electric current. In other words, while it may be satisfactory to treat the electron as a little grain of electricity when it is viewed from afar, the situation is quite different when we zoom in closer.

<sup>&</sup>lt;sup>2</sup>Johannes Diderik van der Waals was awarded the Nobel Prize for Physics in 1910 for his work on the equation of state of gases and liquids. His research on the continuity of fluid states, and in particular gases and liquids, led him to discover short range cohesive forces.

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An electron then looks fuzzy, spreading over several nanometers. Here we have to speak of its wave function, and it looks as though several possible electrons coexist, each being associated with its own position and speed. The phenomena observed have no equivalent in our own world.

The best known of these phenomena is the tunnel effect. In our macroscopic world, if we cut a copper wire carrying a current, this current will no longer pass through it. But this is not quite true on the nanometric scale. If the wire is discontinued over a very tiny distance of the order of a fraction of a nanometer, the electrons arriving at one side of the break already have one 'foot' on the other side. These electrons can then cross the insulating gap. A current passes as though by magic across the gap, although its strength falls off exponentially with the leap it must make. This phenomenon is exploited in scanning tunnelling microscopes (STM). A fine tip is displaced just above a conducting surface, at a distance of a few tenths of a nanometer. A current thus passes with a strength of a few billionths of an ampere, depending sensitively on the tip-surface separation. By displacing the tip and measuring the current at each of its positions, we can thus reconstruct an image of the conductor surface, and we can in a certain sense even 'see' the individual surface atoms. In other situations, the tunnel effect can be something of a nuisance, especially in the manufacture of nanodevices. Indeed, it becomes impossible to use insulators below a certain thickness, simply because a current can then cross them. This is why microscopic transistors in processors or memories are prone to leakage currents which increase the electricity consumption.

Another relevant effect is quantisation. When an electron is trapped in a tiny region of space, it can only exist in a certain number of configurations. There is an analogy with organ pipes. Only sounds of a specific frequency can be emitted from a pipe of given height. This phenomenon, first observed for electrons in atoms, explains why each atom will only emit its own specific spectrum of light. However, the same phenomenon can now be reproduced by enclosing electrons in tiny boxes known as quantum dots. Like atoms, these have specific optical properties.

#### 1.4 How Can We Make Such Tiny Objects?

A nanometer is a truly small length, much shorter than anything that could be perceived by our senses. So how could we possibly make objects on such a scale? Paradoxically, it is rather straightforward, since matter assembles itself spontaneously in nanometric form. For example, if we place a droplet of petrol of a few cubic millimeters on a bowl full of water, it will spread out to form a film a few hundred nm thick. The resulting iridescence is due to the play of light bouncing back and forth from one face to the other of this thin layer of petrol. The surface of a soap bubble may be of similar thickness and the same kind of iridescence is observed.

Even more surprising, in our everyday lives, we produce large amounts of nanoobjects without ever appealing to nanotechnology. The main source of nanoparticles is the combustion of all kinds of materials, such as wood, cigarettes, petrol, and so on, all of which generate vast numbers of nanoparticles. 8 L. Laurent

#### The Nanop Project

This project, which was financed by the *Agence française de sécurité sanitaire de l'environnement et du travail* (AFSSET), was led by researchers from different institutes.<sup>3</sup> Experimental work was carried out in the *maison automatisée pour des recherches innovantes sur l'air* (MARIA), which is an experimental house run by the *Centre scientifique et technique du bâtiment* in Champs-sur-Marne (in the Seine-et-Marne, France). It contains all the standard household goods that a family would use on an everyday basis (see Fig. 1.2). Various devices measure the pollution generated by everyday activities and in each room of the house.

This experimental house was used to analyse nanoparticle emissions produced during daily life, including their concentration, chemical composition, persistence in the air, and propagation throughout the house. This project showed that many such activities do indeed produce these particles, including in particular petrol heating systems and cooking. Peaks of concentration can reach a million nanoparticles per cubic centimeter. These particles propagate extremely quickly from one room to another.



Fig. 1.2 Analysis of particles emitted in the living room. Courtesy of Corinne Mandin, Centre scientifique et technique du bâtiment

<sup>&</sup>lt;sup>3</sup>These include the *Institut national de l'environnement industriel et des risques* (INERIS), the *Centre scientifique et technique du bâtiment* (CSTB), the *Institut de recherches sur la catalyse et l'environnement de Lyon* (IRCELYON), the *Laboratoire d'étude des particules inhalées de la ville de Paris* (LEPI), the *École des hautes études en santé publique* (EHESP), and the *université Paris-Est*.

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In industry, many processes have been developed to produce nano-objects in a controlled way. These fall into three main groups: self-assembly, nanofabrication, and mimicking nature.

#### 1.4.1 Self-Assembly

This first kind of process is useful for making nanoparticles and nanomaterials or treating surfaces. It exploits the tendency of atoms to stick together to form aggregates or even fibres. In scientific jargon, researchers call this the bottom–up approach, because we start out with atoms, at the bottom of the scale, and build structures up from there.

Sometimes when molecules are put in close proximity they assemble spontaneously into aggregates which may be nanometric. This tendency to self-assemble is exploited to fabricate nanoparticles in a great many industrial processes. One can simply heat the right kind of molecule or trigger a chemical reaction so that they break and the resulting pieces will tend to stick to one another. Nanoparticles or fibres produced in this way are then incorporated into a material whose properties one would like to modify, thereby producing a nanomaterial. Another process commonly used in industry is the production of thin films, with thicknesses measured in nanometers. Rather than have the atoms stick to one another, one arranges for them to stick to a surface.

Chemistry is also used to modify the surface of nano-objects such as nanoparticles or nanostructures machined on a surface. Molecules are grafted on to give them specific properties: therapeutic properties for a drug, properties of molecular recognition for diagnosis, and properties of chemical affinity for incorporation into a polymer matrix. The application of this kind of chemistry to nano-objects is referred to as nanochemistry.

#### Nanotrees in the Alps

These are in fact silicon nanostructures which grow on their own in the presence of a vapour containing silicon. The atoms arrange themselves spontaneously into structures with a trunk and 'nanobranches', giving the whole thing the appearance of a fir tree (see Fig. 1.3). These structures are particularly interesting for potential applications in the field of energy storage and energy conversion in photovoltaic cells.