

# Functionalizing carbon nanotubes for nanobiotechnology

A process that exploits the ability of biomolecules to bind and self-organize on the surfaces of carbon nanotubes has been developed to functionalize these nano-objects for nanobiotechnology. This process promises exciting applications such as constructing intelligent drug vector systems, designing biosensors for the assay of biomolecules, and elucidating protein structures.



After chemical synthesis in glass round-bottomed flasks the detergents (lipids) are characterized by nuclear magnetic resonance. They are then mixed with the carbon nanotubes.

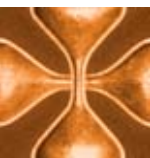
Carbon nanotubes are **micrometric** in length and have diameters in the **nanometre** range (see *Carbon nanotubes: top research performers*). Their remarkable mechanical structural and electrical properties make them attractive for novel applications. Until now they have been studied for a range of applications in nanotechnology including the design of new materials and electronic devices that make use of their high **electron**-carrying capacity, and hydrogen storage.

## Ring-shaped molecular arrangements

Carbon nanotubes take the form of **aggregates** that are insoluble in all solvents. However, **amphiphilic**

**surfactants** (detergents), which combine a charged **hydrophilic** head and a **hydrophobic lipid chain** (fatty acids<sup>(1)</sup>, for example), can be used to prepare water-stable **suspensions**. In these suspensions the detergent chains interact with the **graphite** surfaces of the nanotubes, which are also very hydrophobic, via **Van der Waals bonding**, while the **polar** heads point outwards into the surrounding aqueous

(1) Fatty acid: chain composed of **atoms** of carbon (4 to 24), hydrogen and oxygen. A fatty acid contains a methyl group ( $\text{CH}_3$ ) and its carbon chain, which are not water-soluble (but are liposoluble), and a carboxylic acid group ( $-\text{COOH}$ ), the acid part of the molecule, which is water-soluble (but not liposoluble).



medium. Electron microscope studies (see *Microscopes: first eyes, now also tools*), carried out at the Joliot-Curie Biology Department of the CEA's Life Science Division (DSV), have shown that the treatment of nanotubes using these detergents produces regular striations on the surface of the tubes. The presence of these striations is evidence not only of the **adsorption** of the detergent on the carbon nanotubes, but also of spontaneous molecular self-organization of the surfactant. Earlier work on graphite had already revealed the formation of surface corrugations resulting from an organization into elongated semi-**micelles** forming cylindrical surface structures on the graphite. The same type of effect is probably responsible for the surface features that appear on carbon nanotubes, where ring-shaped arrangements are positioned perpendicular to the tube axis. The occurrence of these rings is observed only when the detergent concentration exceeds the critical micelle concentration, *i.e.*, the concentration below which micelles are not formed spontaneously in the medium. Hence the formation of surface struc-

tures on the nanotubes probably first involves the formation of micelles in solution, which subsequently rearrange into rings. The distance between adjacent rings along the length of the tube is about 30 Å.

## Rings for targeted drug delivery

According to the nature of the fatty acids used, stable rings can be obtained by **polymerization**. This operation takes place by light irradiation (in the **ultra-violet** range) of specially designed detergent **molecules** that incorporate photoreactive groups that can bind with each other. Each detergent molecule can polymerize with two neighbouring molecules to form a lattice network that produces a rigid supramolecular structure. This arrangement is stable and resists repeated organic washing. The **reticulation** of the surfactant lends the rings the cohesiveness that allows them to exist as individual objects when removed from their carbon support. The lipid rings are separated from the nanotube surface by **electrophoresis**, which involves placing the "ringed" nanotubes in an electric field. Because the polar lipid heads are electrically charged, the rings migrate from the carbon nanotubes, forming individualized structures, each with a hydrophobic core and a hydrophilic shell (Figure 1).

These individual ring structures are calibrated according to the tube diameter, which thus acts as a template. The ring cavities provide an environment that is particularly well suited to the incorporation of hydrophobic substances. Such substances, when placed in the core, are rendered water-soluble by the outer hydrophilic coating. This solubility induced by the rings is very useful for the design and construction of drug vectors<sup>(2)</sup> to convey substances with therapeutic activities to predetermined targets in the body. Equipping the outer coating with specifically recognizable motifs allows the targeted delivery of therapeutic compounds. The release of drugs at their target molecules can also be achieved by



A. Gomin/CEA

After mixing and stirring with a detergent, the carbon nanotubes are dispersed by ultrasonication to form stable suspensions.

(2) Vector: a device designed to deliver an active substance to its biological target.

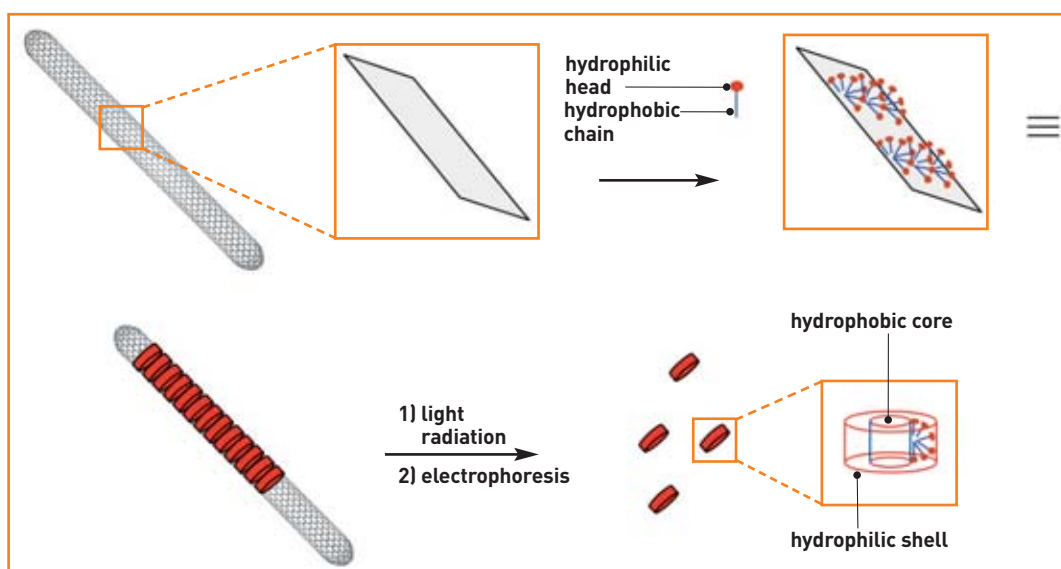


Figure 1. Principle of preparation of lipid nano-rings.



Polymerization of rings around carbon nanotubes by ultraviolet light irradiation to make them rigid.

A. Gonnin/CEA

induced depolymerization of the nano-ring shell: this opens the way to new “intelligent” vector systems.

### Proteins organized in a helical arrangement

Carbon nanotubes possess a perfectly defined regular tubular structure, with a high specific surface<sup>(3)</sup>. These properties make them an ideal material for studying interactions with biomolecules, such as fatty acids and **proteins**. Streptavidin was selected as a model for the study of the **self-assembly** of proteins on carbon nanotubes. This tetrameric protein, *i.e.*, composed of four associated units, is produced by the **bacterium** *Streptomyces avidinii*. The choice of multi-walled carbon nanotubes (MWNTs) for the crystallization of proteins was made because these tubes present a wide distribution of diameters, which enables proteins to find the diameter that best fits their helical crystallization. When the nanotubes are placed in contact with molecules of streptavidin in an aqueous medium, inspection of the sample under an electron microscope shows that in most cases the protein binds randomly to the tube surface. However, ordered arrangements of streptavidin were observed in the form of regular striations along the tube. These striations, spaced 64 Å apart and inclined at an angle of 71° to the axis of the tube, show helical crystallization of the protein, which self-organizes into eight protein units per turn of the helix (Figure 2). The organization of streptavidin at the surface of the nanotubes is assisted by the presence of hydrophobic domains in the protein structure, which allow it to interact with the graphite layer of the carbon nanotubes. These properties had already been exploited

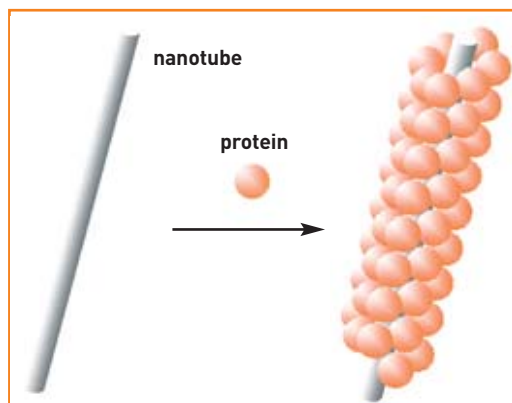


Figure 2. Self-assembly of proteins on a carbon nanotube.

for the purification of the protein on hydrophobic resin columns.

### A source of information to help resolve protein structure

The setting up of an organized helical system of proteins is of special interest for structural studies using microscopy. This type of arrangement makes it possible to observe the protein from many angles, and to extract, from a single microscope view, the information necessary to visualize its three-dimensional structure. The morphology of the **crystals** obtained by this method is consistent with that demonstrated by other conventional systems used for elucidating protein structures (**X-ray diffraction** or **nuclear magnetic resonance**). The helical crystallization of proteins on carbon nanotubes supplies structural information with a **resolution** of 25 Å. The same type of arrangement has been observed with other protein systems, *e.g.*, HupR<sup>(4)</sup>, which also organizes spontaneously in a helical pattern along the nanotube.

### Attractive perspectives

In addition, besides its interest for structural biology, the helical organization of proteins on carbon nanotubes can also serve as a basis for the design of biosensors. Biochemical nano-**electrodes** can be made from an organized monolayer of proteins specific to a particular **ligand**. The disturbance induced by the binding of this ligand produces a signal that is relayed by the carbon nanotubes towards a suitable detection system. The nanosensor allows the transmission and analysis of the data by converting the biochemical signals into electronic pulses. The use of carbon nanotubes to build biosensors lowers sensitivity thresholds and at the same time allows detection systems to be further miniaturized.

In addition, obtaining amphiphilic nano-rings on carbon nanotubes opens up perspectives for new mole-



CEA-IGBMC

Three-dimensional structure of streptavidin reconstituted from electron microscope images.

(3) Specific surface: developed surface of a solid per unit mass.

(4) HupR is a protein involved in the response of the photosynthetic bacterium *Rhodospirillum rubrum* to hydrogen.



cular vector nanosystems. The synthesis, by the methods of organic chemistry, of surfactants specifically designed to create a cohesive supramolecular assembly stabilizes the nanovector when it is removed from its carbon template. These lipid nano-rings favour the accurately targeted delivery of chemical entities with therapeutic activities.

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## From nano-objects to macrocomponents: sol-gel nanomaterials for optics

The capacity to synthesize organic-inorganic hybrid materials by the sol-gel route opens up new perspectives for the development of nanomaterials with specific properties. For the optical components of the high-power lasers in its Simulation Program for replacement of thermonuclear weapons testing, the CEA has developed coatings made of hybrid materials of this type. These materials are used to produce reflective layers for mirrors and anti-oxidation protection for the metal surfaces of amplifiers. Novel approaches of this type can also be used to make nanomaterials with a hierarchical organization that display special properties in fields other than optics.

Coating of an optical component of the LMJ (Megajoule Laser) by the sol-gel process. The solution to be deposited is synthesized in a 300 litre tank. The optical component is dipped in the bath and removed at a constant rate to ensure controlled deposition of the coating.



CEA

**T**he molecular construction of organic-inorganic hybrid materials makes it possible to conceive and engineer tailor-made structures (*Lego™ Chemistry*). The inorganic parts offer the functions that are classically associated with mineral compounds, namely mechanical strength, chemical inertness, heat resistance, optical properties, electrical

properties, etc. The organic parts provide mechanical cohesion (structure, matrix), plasticity, adhesiveness and transparency, etc.

The Sol-Gel Laboratory in the Materials Department (Département Matériaux) of the Military Applications Division (CEA/Le Ripault) is particularly interested in nanomaterials, as part of its Simulation Program

for thermonuclear weapons, designed to enable France to conserve its deterrent capability after the permanent halt of nuclear explosion testing, for the development of new generations of optical coatings for high-power lasers.

### Hybrid materials produced by soft chemistry

The **sol-gel**<sup>(1)</sup> technique is used to make inorganic or organic-inorganic hybrid materials by means of liquid-phase molecular reactions at temperatures much lower than those used in conventional processes, whence the term **soft chemistry**. The starting point for the synthesis is a mixture of ionic (salts) and/or molecular (alkoxides<sup>(2)</sup>) precursors in solution, called a *sol*, in which chemical reactions of inorganic **hydrolysis** and **polymerization** take place, ultimately producing a network made up of a highly viscous medium called a *gel*, or a **colloidal** system that favours the **nucleation** of chemical species and their controlled growth.

A colloidal **suspension** consists of a solid phase with a **particle size distribution** in the range 1 **nanometre** to 1 **micrometre**, dispersed in a liquid. The rheological stability<sup>(3)</sup> of this dispersion is maintained by the presence of an identical surface electric charge on all the particles. This electric charge is set by the **catalytic** conditions of the reaction medium and is linked to the **pH** of the medium. From a stable dispersion of extremely pure **silicon** oxide (or silica), it is possible to obtain a particulate gel or a **precipitate** by neutralizing the electric charge and thereby reaching the zero-charge point.

### Varied preparation strategies

The molecular approach to the sol-gel synthesis readily permits the association of different precursors of inorganic or organic origin, and thus allows the preparation of hybrid materials<sup>(4)</sup>. Two types of hybrid materials can be synthesized, and a classification according to the nature of the interactions between the inorganic and organic phases has been proposed. *Class I hybrids* are systems in which the organic component (**molecule**, oligomer<sup>(5)</sup> or **polymer**) is simply trapped in an inorganic network. The interactions between inorganic and organic components are weak (**Van der Waals forces**, **hydrogen bonds** or **electrostatic interactions**). *Class II hybrids* are materials in which the organic and inorganic components are chemically linked by a strong **bond**, which can be either **covalent** or **ionocovalent**.

According to the branch of chemistry they work in, chemists preparing hybrid materials adopt different strategies. *Solid phase chemists* use intercalation chemistry<sup>(6)</sup>, lamellar networks (clays, phosphates, etc.), **templating** based on the use of organic structuring agents (**amines**, alkylammonium ions, **surfactants**, etc.) to build a hybrid material. *Polymer chemists* make use of macromonomers or organic polymers to structure the material and introduce inorganic charges to modulate the resulting properties. The ease with which a hybrid material is obtained depends essentially on the quality of the interface between the two phases, which determines the homogeneity,

and so the performance, of the final material. Appropriate functionalization of the polymer makes it possible to improve the mutual dispersion of the two components. *Sol-gel chemists* use various methods of synthesis such as impregnation of porous mineral phases, the use of preformed entities (**aggregates**, metal colloids, oxides) or the use of heterofunctional metal alkoxides to favour copolymerization of inorganic and organic phases.

### Developing hybrid materials for optical coating

For more than 30 years the CEA has been engaged in the laboratory study of **plasmas** produced by the interaction of high-power pulse lasers with matter. The successive high-power installations (Phébus, LIL, LMJ) are based on a solid glass laser **doped** with neodymium, with high-aperture optics.

The Megajoule Laser (LMJ: Laser Mégajoule) under construction at the Aquitaine Scientific and Technical Research Centre (Cesta: Centre d'études scientifiques et techniques d'Aquitaine) near Bordeaux, will be made up of 240 square-geometry unit beams with aperture 40 x 40 cm<sup>2</sup>. The laser pulse will travel about 450 m and pass through or be reflected from dozens of optical components. To reduce energy losses, prevent damage to optics due to interference reflection on the dioptres<sup>(7)</sup> and direct the laser pulse onto the target, 10,000 m<sup>2</sup> of optical coatings with high laser resistance is planned. More than 96% of this treated surface consists essentially of anti-reflection and reflective layers. Among the materials that make up the coatings, hybrid materials have been specifically developed for this purpose.

### A reflective coating for cavity mirrors

For reasons of laser resistance, metal mirrors, which significantly absorb wavelengths of interest, cannot be used for this laser application. The mirrors used are therefore composed of transparent **multidielectric** substances (insulating oxides). They are made up of stacked superimposed deposition layers in which low and high **refractive index** materials alternate. The coefficient of reflection of the mirror depends on the ratio of the indices of these component materials and the number of unit layers laid

(1) C. J. BRINKER and G. W. SCHERER, *Sol-Gel Science*, Academic Press, New York, 1990.

(2) Alkoxide: organometallic compound with formula  $M(OR)_n$  where M is the cation (positive ion) of a metal or metalloid (non-metallic element), R is an organic group and  $n$  the coordination number of M, i.e., the number of nearest neighbours.

(3) Rheology: the study of the deformation and flow properties of materials, measured by their viscosity, elasticity and plasticity.

(4) P. GOMEZ-ROMERO and C. SANCHEZ, *Functional Hybrid Material*, Wiley-VCH, Weinheim, 2004.

(5) Oligomer: molecule of intermediate molar mass, the structure of which is essentially made up of repeats of a small number of units derived from molecules of low molar mass.

(6) Intercalation chemistry: chemistry generating continuous open structures that allow the reversible incorporation of chemical species (ions, H<sub>2</sub>O, etc.).

(7) Dioptre: surface separating two media with different refractive indices.

down. In this way, using about 20 layers, reflectivity values of about 99% can be achieved.

The cavity mirror of the LMJ or the Laser Integration Line (LIL: Ligne d'intégration laser), a prototype installation of one of LMJ chains, is equipped with a novel deformable substrate that corrects the wave surface of the beam, thus limiting optical aberrations<sup>(8)</sup> induced each time a component is traversed. In this particular case, the use of a coating composed of stress-free sol-gel layers greatly helps to resist substrate distortions caused by this correction phase.

To allow the construction of a reflective coating on a deformable support from materials based on **nanoparticles**, it is important to develop a colloidal layer with a high refractive index. One way to increase the index of colloidal layers is to include in the suspen-

sion a soluble polymer binder, such as PVP (polyvinylpyrrolidone). By increasing the binder content in a colloidal system, chemists raise the refractive index of the film. The binder/oxide mass ratio will determine the refractive index of the hybrid, and therefore that of the corresponding thin film (Figures 1a and 1b).

In addition, the study of the **steric** arrangement of the polymer with zirconium colloids ( $ZrO_2$ ) has revealed that for the optimum ratio, PVP occupies the space around the oxide colloids by forming hydrogen bonds between the pyrrolidone carbonyl functions and hydroxyl groups (OH) at the surface of the  $ZrO_2$  (Figure 1c). By this grafting, colloids and polymers form a much denser hybrid compound (the residual porosity is estimated at about 17%). To construct the multielectric mirrors of the LMJ, the materials that compose the reflective stack are  $ZrO_2$ -PVP for high refractive index and colloidal silica  $SiO_2$  for low refractive index.

The homogeneity of the coating is satisfactory and meets specifications using a low temperature process that is compatible with deposition on a deformable substrate. Concerning the requirement for laser resistance, measurements were made on representative samples of size 200 x 200 mm<sup>2</sup> (600 measurement sites). The results validate the materials and the stacking used: the mean laser flux tolerance was 18.3 J/cm<sup>2</sup> (the specification for this optical component was 7 J/cm<sup>2</sup>).

### A protective coating for metal components

The amplifying cavities of the LMJ contain large reflective metal parts (1,800 x 635 mm<sup>2</sup>). These silvered reflectors are used to reflect the light emitted by flash lamps to increase the **pumping** efficiency of the laser glass slabs. As the amplifying cavity of the laser works under airflow, the silvering of these parts undergoes strong **oxidation**, which greatly reduces the lifespan of the components. The development of a protective coating is therefore essential.

The use of the sol-gel process to construct protective coatings on metals is known. However, in the present case, it is also necessary to conserve as well as possible the reflective power of the silvering. For that purpose a barrier film that is transparent in the spectral domain (400-1,000 nm) is necessary. To meet this need, an organic-inorganic hybrid material based on polymeric silica and organically modified silica (using organosilicate precursors) has been developed. This material, which takes the form of a very thin film (a few nanometres thick), provides an efficient protection against oxidation while conserving a reflective power greater than 90% at 500 nm (**specular reflection**).

A prototyping step on a representative part recently demonstrated the feasibility of the protection treatment. A test of the efficiency of the protection coating in operational conditions has validated this process, and in particular the stability of the

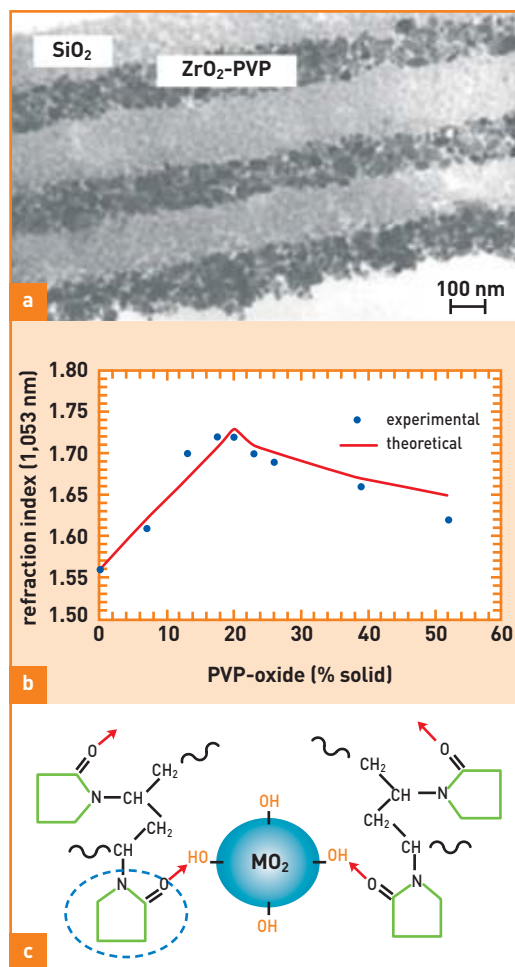
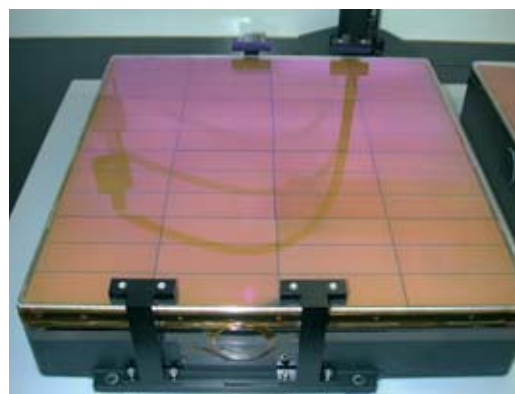


Figure 1. Sol-gel reflective coating based on organic-inorganic hybrid nanomaterials with a coefficient of reflection greater than 99% (1,053 nm).

a: transmission electron microscope observation of  $SiO_2/ZrO_2$ -PVP multilayer stacking.  
b: experimental variations (points) and theoretical variations (unbroken line) of the refractive index of a hybrid  $ZrO_2$ -PVP mixture according to the quantity of polymer.  
c: types of interaction between PVP and a colloidal oxide  $MO_2$ . The blue dotted line encircles a pyrrolidone carbonyl function.

Deformable mirror at the end of the LIL amplifying cavity treated with a sol-gel reflective coating with a coefficient of reflection greater than 99% (1,053 nm). The coating consists of a stack of  $ZrO_2$ -PVP, a material with a high refractive index ( $n_{1,053\text{ nm}} = 1.72$ ), and colloidal silica  $SiO_2$ , a material with a low refractive index ( $n_{1,053\text{ nm}} = 1.22$ ).



(8) Optical aberration: effect causing a deterioration of image quality in an optical system. For example, in spherical and cylindrical mirrors spherical aberration prevents all the incident rays parallel to the main axis converging to the focal point.

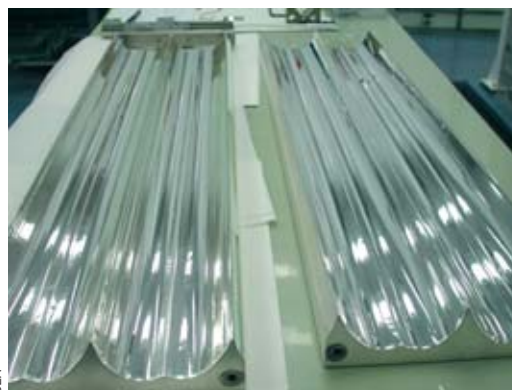
material after 12,742 pulses from flash discharge lamps<sup>(9)</sup>.

### Novel concepts for optical coatings

Among the new hybrid materials that have recently appeared are materials with a hierarchical structure, *i.e.*, materials with several levels of dimensional organization, characterized by a multiscale porosity network. The hierarchy in these constructions is achieved by the organization and stacking of elementary objects in series or in parallel by **self-assembly**, co-assembly or direct assembly. The process starts with the construction of these units, continues with their assembly into more elaborate objects and ends with a complex hierarchical structure. Such constructions are ubiquitous in naturally-occurring materials such as wood and bone. These natural materials often exhibit specific properties that lend them exceptionally high performance in their domains of application (one gram of bone has a compression stability four times higher than one gram of steel!).

The synthesis of hierarchical materials requires more advanced work in molecular chemistry, and especially in interface chemistry. In general, the synthesis strategies use materials that serve as templates, which by their size and composition set the pore dimensions, and so define the intrinsic end architecture of the material. The porosity domains studied range from micropores to macropores *via* mesopores. Combining these different sizes opens the way to the construction of materials with multimodal porosity. The possibilities offered by the “nano-engineering” of objects displaying specific organization in size ranges between the **ångström** and the centimetre are limited only by the multiple combinations and affinities that can exist between organic and inorganic materials. The enthusiasm elicited in recent years by the synthesis of **mesostructured** materials by the sol-gel process is evidence of the high value of these structures and their properties.

Mesostructured phases are readily synthesized with the help of surfactants that in liquid media self-organize



Silvered reflector of the LMJ. A coating made of a very thin film of organic-inorganic hybrid material constructed by the sol-gel process was developed to protect it efficiently against oxidation, while at the same time retaining as much as possible of its reflecting power.

into **micelles**, and at longer range into liquid crystals (Figure 2a). Using the micellar organization of these organic phases in **polar** solvents such as water or alcohols to support and control the growth of oxide networks by hydrolytic polycondensation of metal alkoxides permits the development of **nano-structured** materials. These nanomaterials form a very well-defined network, the structural parameters of which are directly linked to the nature of the surfactant and its ability to form micellar phases in the appropriate solvent. The elimination by chemical or thermal means of this surfactant, which is trapped inside the inorganic network thus created, releases the porosity of the system, characterized by a calibrated pore size, or even a **crystalline** structure corresponding to a space group.

In order to generate new structures for materials suitable for optical applications, researchers at the Sol-Gel Laboratory have developed hybrid nanomaterials that are the first example of the construction of hybrid mesostructured phases produced *in situ* inside a non-pore-forming polymer matrix called a “host” polymer (Figure 2b).

The use of these nanomaterial solutions has thus provided transparent films of low refractive index through this new growth process for a mesostructured organomineral phase inside an organic host polymer matrix. Photographs of these types of coating, obtained by electron microscopy at macroscopic or nanometric scales, reveal the hierarchical structure of the material (Figure 3). They give a visual illus-

(9) P. BELLEVILLE, P. PRENÉ, C. BONNIN and Y. MONTOULLIOUT, “Use of sol-gel hybrids for laser optical thin films”, *Mat. Res. Soc. Symp. Proc.*, 726, 2002.

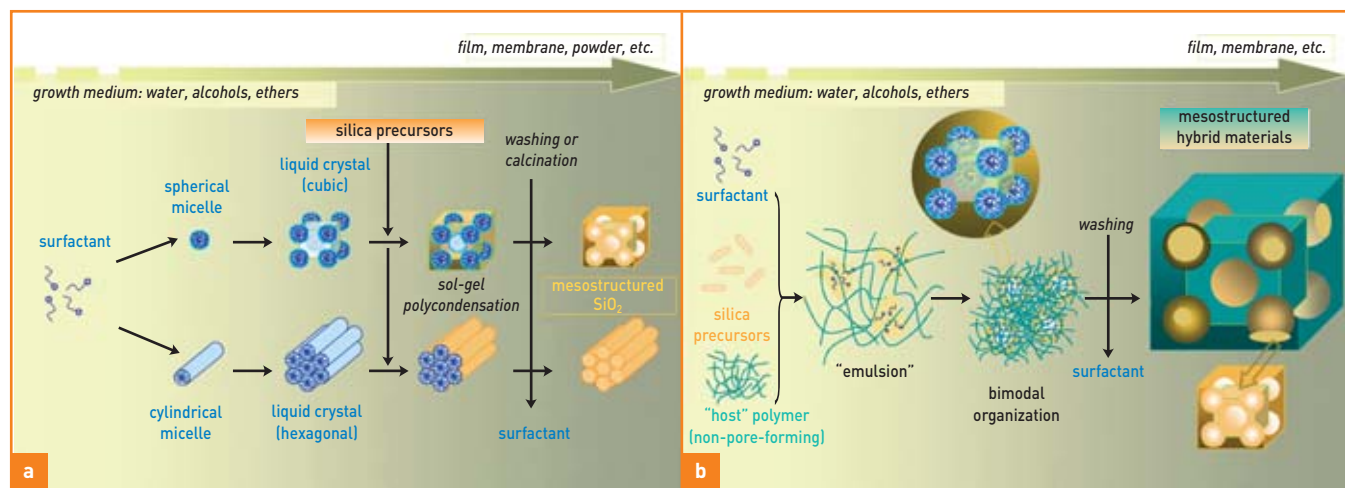


Figure 2. Growth by the sol-gel process and evaporation-induced self-assembly. a: mesostructured phases; b: structured hierarchical materials.

tration of the growth inside an organic polymer of calibrated micron-sized inorganic spheres with a nanostructured inorganic network.

It is possible to totally modify the macroporous organization of such structures by exploiting the compatibility between the different constituents of the reaction medium (solvent/surfactant/polymer/metal oxide). Thus by simply changing solvent or template (surfactant) and keeping the same polymer-silica pair, mesoporous films with a high sponge-like porosity (Figures 4a and 4b) and other mesoporous materials with no apparent macroscopic porosity (Figure 4c) have been prepared at the CEA. These films keep their transparency, and therefore a homogeneous refractive index, with compositions rich in both inorganic and organic constituents (level of incorporation of silica greater than 40% by weight). These hybrid constructions give access to new hybrid nanomaterials with a hierarchical organization, the

properties of which are at present being assessed at the Sol-Gel Laboratory. One current research direction is the development of optical coatings that are equally resistant to laser flux, but less sensitive to molecular pollution<sup>(10)</sup>, for the purpose of increasing the lifespan of these materials used on high-power laser chains.

## Promising nanomaterials

Besides finding applications in optics, these hybrid nanomaterials are also being studied for their many other interesting properties; electrochemical (**electrolytic** membranes, electrochromic<sup>(11)</sup> and photo-voltaic devices), electronic (**capacitive**, ferroelectric<sup>(12)</sup> and **piezoelectric** films), magnetic and biological (biogels, biosensors). These few examples of applications show that the rich capacities of the chemistry of the sol-gel precursors and the possibility of "nano-engineering" desired materials, offer obvious potential for the construction of new materials based on innovative approaches and the technology of tomorrow.

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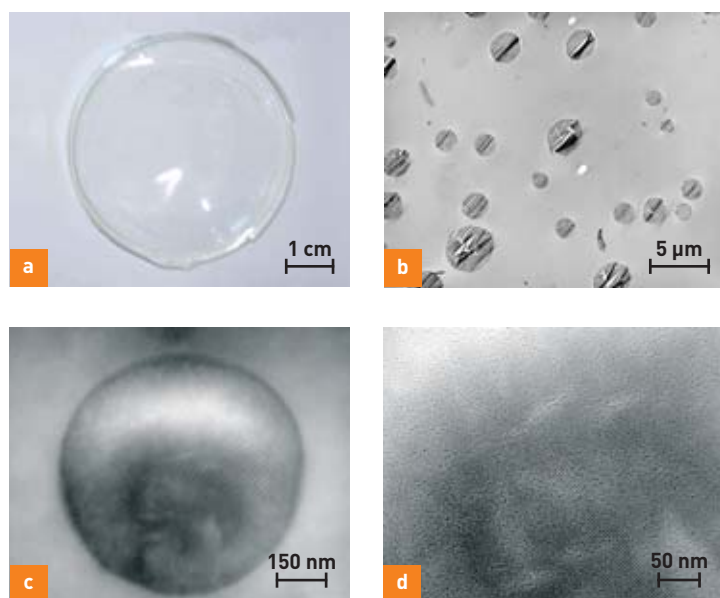


Figure 3. Electron microscopy images at different scales of a transparent film of an organic-inorganic hybrid material with multi-scale organization synthesized by the growth of nanostructured spherical particles of silica inside an organic polymer. Photographs: macroscopic (a); microscopic (b); nanoscopic (c); subnanoscopic (d).

(10) Molecular pollution: pollution consisting of molecules picked up by migration through contact with assembly joints or airborne migration (e.g., volatile organic compounds from degassing).

(11) Electrochromic: possessing light-transmitting properties that vary according to an applied electrical voltage.

(12) Ferroelectric: presenting a spontaneous electrical polarization that is reversible through the action of an external electric field.

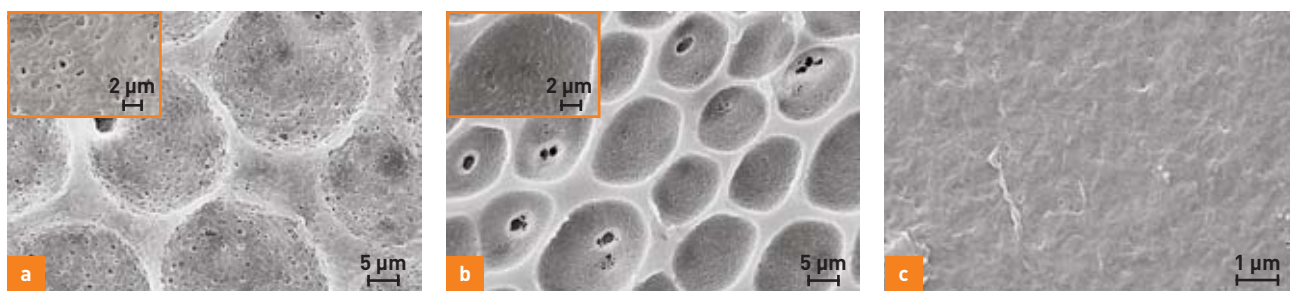


Figure 4. Electron microscope photographs showing the hierarchical organization of transparent films constructed by the sol-gel process and by self-assembly in a "host" polymer medium. Films formed with; a: an ionic surfactant and tetrahydrofuran, b: a non-ionic surfactant and acetone, c: a non-ionic surfactant and tetrahydrofuran.



# A From the macroscopic to the nanoworld, and vice versa...

In order to gain a better idea of the size of microscopic and nanoscopic\* objects, it is useful to make comparisons, usually by aligning different scales, *i.e.* matching the natural world, from molecules to man, to engineered or fabricated objects (Figure). Hence, comparing the “artificial” with the “natural” shows that artificially-produced **nanoparticles** are in fact smaller than red blood cells.

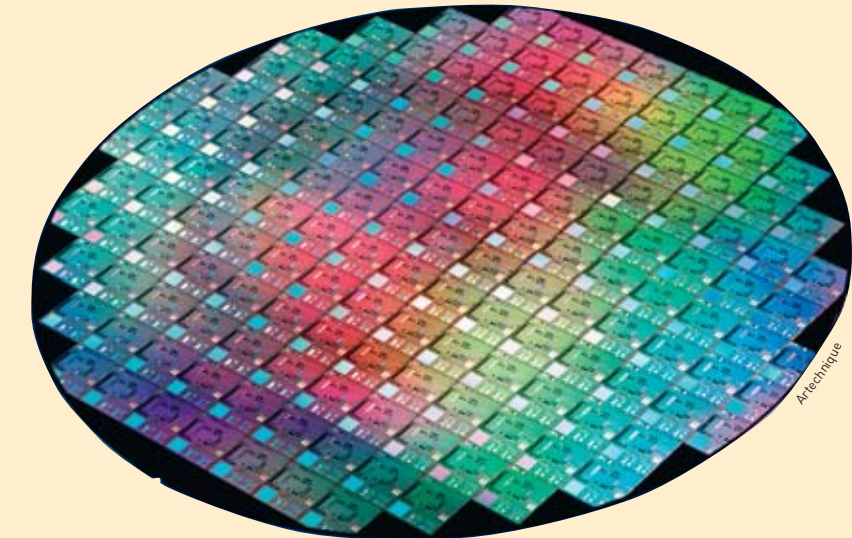
Another advantage of juxtaposing the two is that it provides a good illustration of the two main ways of developing nanoscale systems or objects: **top-down** and **bottom-up**. In fact, there are two ways

\* From the Greek *nano* meaning

“very small”, which is also used as a prefix meaning a billionth ( $10^{-9}$ ) of a unit.

In fact, the **nanometre** ( $1 \text{ nm} = 10^{-9}$  metres, or a billionth of a metre), is the master unit for nanosciences and nanotechnologies.

into the nanoworld: molecular manufacturing, involving the control of single **atoms** and the building from the ground up, and extreme miniaturization, generating progressively smaller systems. Top-down technology is based on the artificial, using macroscopic materials that we chip away using our hands and our tools: for decades now, electronics has been applied using **silicon** as a substrate and what are called “**wafers**” as workpieces. In fact, microelectronics is also where the “top-down” synthesis approach gets its name from. However, we have reached a stage where, over and above simply adapting the miniaturization of silicon, we also



300-mm silicon wafer produced by the Crolles2 Alliance, an illustration of current capabilities using top-down microelectronics.

have to take on or use certain physical phenomena, particularly from **quantum** physics, that operate when working at the nanoscale.

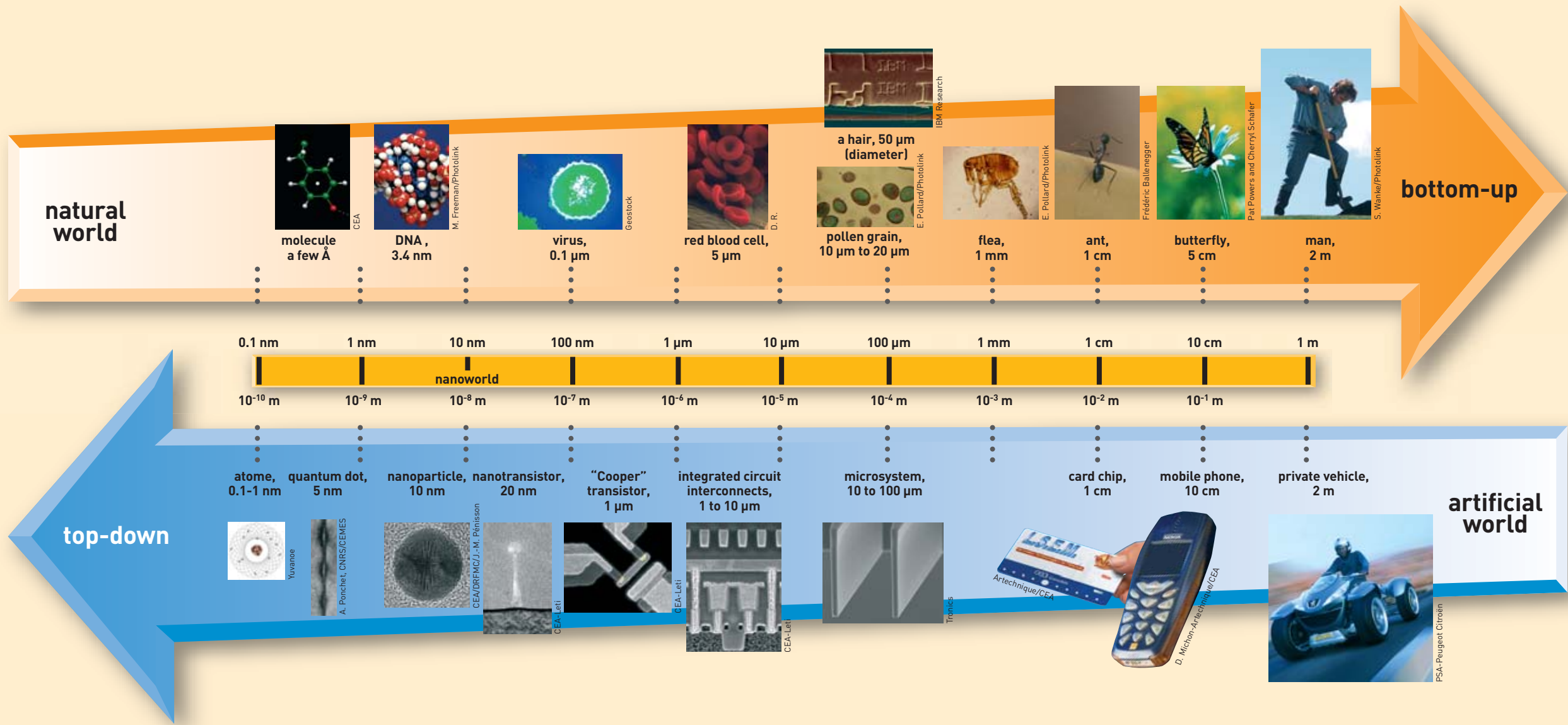
The bottom-up approach can get around these physical limits and also cut manufacturing costs, which it does by using component **self-assembly**. This is the approach that follows nature by assembling molecules to create **proteins**, which are a series of amino acids that the super-molecules, *i.e.* **nucleic acids** (**DNA**, **RNA**), are able to produce within cells to form functional structures that can reproduce in more complex patterns. Bottom-up synthesis aims at structuring the material using

“building blocks”, including atoms themselves, as is the case with living objects in nature. Nanoelectronics seeks to follow this assembly approach to make functional structures at lower manufacturing cost.

The **nanosciences** can be defined as the body of research into the physical, chemical or biological properties of nano-objects, how to manufacture them, and how they self-assemble by auto-organization.

**Nanotechnologies** cover all the methods that can be used to work at molecular scale to reorganize matter into objects and materials, even progressing to the macroscopic scale.

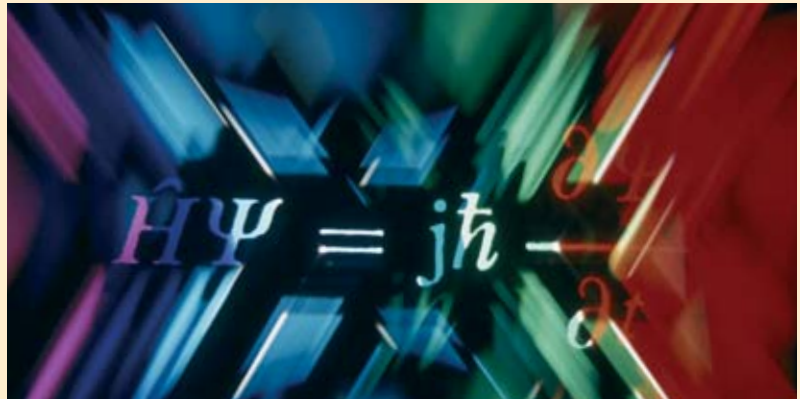
A (next)



## B A guide to quantum physics

**Q**uantum physics (historically known as quantum mechanics) covers a set of physical laws that apply at microscopic scale. While fundamentally different from the majority of laws that appear to apply at our own scale, the laws of quantum physics nevertheless underpin the general basis of physics at all scales. That said, on the macroscopic scale, quantum physics in action appears to behave particularly strangely, except for a certain number of phenomena that were already curious, such as **superconductivity** or superfluidity, which in fact can only be explained by the laws of quantum physics. Furthermore, the transition from the validating the paradoxes of quantum physics to the laws of classical physics, which we find easier to comprehend, can be explained in a very general way, as will be mentioned later.

Quantum physics gets its name from the fundamental characteristics of quantum objects: characteristics such as the angular momentum (**spin**) of **discrete** or discontinuous particles called **quanta**, which can only take values multiplied by an elementary *quantum*. There is also a **quantum of action** (product of a unit of energy multiplied by time) called **Planck's cons-**



D. Sarrault/CEA

An "artist's impression" of the Schrödinger equation.

**tant** (symbolized as  $h$ ) which has a value of  $6.626 \times 10^{-34}$  joule-second. While classical physics separates *waves* from *particles*, quantum physics somehow covers both these concepts in a third group, which goes beyond the simple wave-particle duality that Louis de Broglie imagined. When we attempt to comprehend it, it sometimes seems closer to waves, and sometimes to particles. A quantum object cannot be separated from how it is observed, and has no fixed attributes. This applies equally to a particle - which in no way can be likened to a tiny little bead following some kind of trajectory - of light (**photon**)

or matter (**electron, proton, neutron, atom**, etc.).

This is the underlying feature behind the **Heisenberg uncertainty principle**, which is another cornerstone of quantum physics. According to this principle (which is more *indeterminacy* than *uncertainty*), the position and the velocity of a particle cannot be measured *simultaneously* at a given point in time. Measurement remains possible, but can never be more accurate than  $h$ , Planck's constant. Given that these approximations have no intrinsically real value outside the observation process, this simultaneous determination of both position and velocity becomes simply impossible.

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At any moment in time, the quantum object presents the characteristic of *superposing* several states, in the same way that one wave can be the *sum* of several others. In quantum theory, the amplitude of a wave (like the peak, for example) is equal to a **probability amplitude** (or probability wave), a complex number-valued function associated with each of the possible states of a system thus described as quantum. Mathematically speaking, a physical state in this kind of system is represented by a **state vector**, a function that can be added to others *via* superposition. In other words, the sum of two possible state vectors of a system is *also* a possible state vector of that system. Also, the product of two vector spaces is also the sum of the vector products, which indicates **entanglement**: as a state vector is generally spread through space, the notion of local objects no longer holds true. For a pair of entangled particles, *i.e.* particles created together or having already interacted, that is, described by the *product* and not the *sum* of the two individual state vectors, the fate of each particle is linked - entangled - with the other, regardless of the distance between the two. This characteristic, also called *quantum state entan-*

*glement*, has staggering consequences, even before considering the potential applications, such as quantum cryptography or - why not? - teleportation. From this point on, the ability to predict the behaviour of a quantum system is reduced to probabilistic or statistical predictability. It is as if the quantum object is some kind of "juxtaposition of possibilities". Until it has been measured, the measurable size that supposedly quantifies the physical property under study is not strictly defined. Yet as soon as this measurement process is launched, it destroys the **quantum superposition** through the "collapse of the wave-packet" described by Werner Heisenberg in 1927. All the properties of a quantum system can be deduced from the equation that Erwin Schrödinger put forward the previous year. Solving the **Schrödinger equation** made it possible to determine the energy of a system as well as the **wave function**, a notion that tends to be replaced by the probability amplitude.

According to another cornerstone principle of quantum physics, the **Pauli exclusion principle**, two identical half-spin ions (**fermions**, particularly electrons) cannot simultaneously share the same position, spin and velocity (within

the limits imposed by the uncertainty principle), *i.e.* share the same *quantum state*. **Bosons** (especially photons) do not follow this principle, and can exist in the same quantum state.

The coexistence of **superposition states** is what lends **coherence** to a quantum system. This means that the theory of **quantum decoherence** is able to explain why macroscopic objects, atoms and other particles, present "classical" behaviour whereas microscopic objects show quantum behaviour. Far more influence is exerted by the "environment" (air, background radiation, etc.) than an advanced measurement device, as the environment radically removes all *superposition of states* at this scale. The larger the system considered, the more it is coupled to a large number of degrees of freedom in the environment, which means the less "chance" (to stick with a probabilistic logic) it has of maintaining any degree of quantum coherence.

### TO FIND OUT MORE:

Étienne Klein, *Petit voyage dans le monde des quanta*, Champs, Flammarion, 2004.