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# Nanogeometry

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**Abstract**

Nanosciences and nanotechnology (NST) currently constitute a major research field all over the world. NST deal with the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at the larger scale. The properties of materials can be different at the nanoscale for two main reasons: size and quantum effects. In this work, some effects of geometry at the nanoscale are considered: enhanced specific area, adsorption, chemical reactivity. The cases of nanocrystals, fullerenes and carbon nanotubes are studied.

## Introduction

Nanosciences and nanotechnology (NST) currently constitute a major research field [1–3] all over the world. NST are believed to lead to dramatic modifications of many of our activities: technologies of information and communication, materials, energy, space, medicine, water, etc. NST include elements of mechanics, thermodynamics, electricity, quantum mechanics, geometry, etc. Although the field of NST is pluridiciplinary, it is possible to introduce some basic notions in various courses [4]. For instance, scaling laws may help to understand the differences between the macro-, micro- and nanoworlds [5, 6].

As defined by the Royal Society [7]: nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at the larger scale. Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometre scale. The characteristic dimensions where properties differ significantly from those at the larger scale are generally in the 10 nm range, for geometric, cohesive, thermal and electronic properties [8].

The properties of materials can be different at the nanoscale for two main reasons. First, nanomaterials have a relatively large surface area when compared to the same mass of material produced in a larger form. This can make materials more chemically reactive (in some cases

  

materials (like gold) that are inert in their larger form are reactive when produced in their nanoscale form) [9], and affect their strength or electrical properties. Second, quantum effects can begin to dominate the behaviour of matter at the nanoscale affecting the optical, electrical and magnetic behaviour of materials.

When looking at the nanoworld, there exist two main approaches. In the 'top-down' approach, one looks at the variation of the properties of systems that change when going from the macroscopic to the nanoscopic dimensions. This allows us to use well-known scientific laws and to extrapolate to small dimensions. The usefulness of scaling laws is demonstrated here. At the opposite, in the 'bottom-up' approach, one starts from atoms and/or small molecules, and one adds more and more atoms, in order to see how the properties are modified.

Here we restrict ourselves to nanogeometry, i.e. the geometric properties of nanosystems. The influence of nanogeometry on some physical and chemical properties of nanosystems are also discussed.

For teaching purposes, the subject has some advantages:

- it shows that geometry also applies at the nanometer and atomic scales;
- it uses the fact that atoms have a geometrical shape;
- it shows that geometry influences the chemical and physical properties, and that mathematics (via geometry), physics and chemistry are interrelated;
- it shows how simple topological rules may determine relevant properties of a physical or chemical nature;
- it is appropriate to undergraduate students of chemistry, physics, materials science and materials engineering who want to understand how a new class of molecules and materials can find important applications in different areas of (nano-)technology;
- it shows how simple reasoning and basic scientific notions are useful to understand modern science.

In the following, we use the 'top-down' approach in order to study so-called size effects. The cases of fullerenes and carbon nanotubes are also treated.

## From the macro- to the nanoworld: the 'top-down' approach

Let us use the 'top-down' approach, in order to study some effects of size. In the first example, let us examine how the specific area of particles varies when their linear dimension varies.

Let us take a cube with sides of length $C$ (figure 1), with volume $V = C^3$. The total area of its six faces is equal to $A_1 = 6 \cdot C^2$. Let us divide the cube into $2^3 = 8$ identical cubes. The total volume remains constant. However, the total area of the faces is now equal to $A_2 = 2 \cdot A_1 = 12 \cdot C^2$. Similarly, when the initial cube is divided $n$ times into identical small cubes, the total volume is constant, while the total area of the faces varies like $A_n = n \cdot A_1$.

Altogether, the total surface to volume ratio varies like

$$A_n/V = 6 \cdot n/C. \tag{1}$$

The ratio $A_n/V$ is called the 'specific area', when $V$ is a unit volume. It turns out that the specific area increases when the size of the nanoparticles decreases.

This size effect is important in phenomena taking place at the surface of solids (adsorption, heterogeneous catalysis, etc).

### *The specific area of nanopowders*

Let us evaluate the specific area of a powder (of mass equal to 1 g) made of carbon spherical nanoparticles, with radius $r = 10$ nm. The density of carbon is equal to $\rho = 2.26$ g cm$^{-3}$. In

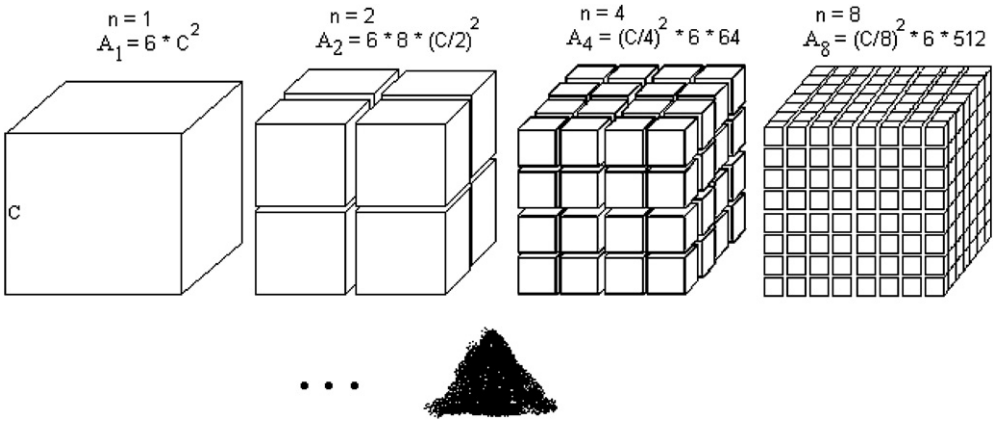


**Figure 1.** The specific area varies with the size of the cubes, at constant volume.

the case of spheres, the ratio $A/V = (4\pi r^2)/(4\pi r^3/3) = 3/r$. Here, $A/V = 3 \times 10^8$ m$^2$ m$^{-3}$. One easily calculates that the specific area is equal to 0.133 km$^2$ kg$^{-1}$ = 133 m$^2$ g$^{-1}$. This principle is currently used in gas masks, so-called sorption pumps and heterogeneous catalysis.

### *Adsorption on nanopowders*

For instance, at low temperature, nitrogen may be adsorbed on nanoparticles. Let us calculate the amount of nitrogen adsorbed on 1 kg of carbon nanoparticles. From the literature, the area of one nitrogen molecule is equal to 0.162 nm$^2$. A simple calculation gives the number of nitrogen molecules adsorbed: $0.82 \times 10^{24}$ nitrogen molecules.

Given that at standard pressure and room temperature, one mole of gas occupies a volume of 22.4 L, one deduces that 32 L of nitrogen are adsorbed on 1 kg of carbon nanoparticles.

## Nanocrystals

Geometrical objects made of closed faces satisfy the generalized Euler relation, namely

$$F - A + S = K$$

where $F$, $A$ and $S$ are the numbers of faces, edges and summits, respectively. $K$ is the Euler characteristics and is related to the number of holes, $g$ (for genus), via $K = 2(1 - g)$ [10]. For a torus, $g = 1$. For polyhedra, $g = 0$.

Nanoparticles are often observed as being regular polyhedra. In many cases, these are so-called Platonic polyhedra: cube, octahedron, decahedron, dodecahedron, icosahedron [11]. These polyhedra satisfy the well-known conventional Euler relation, namely

$$F - A + S = 2. \tag{2}$$

The values of $F$, $A$ and $S$ for different polyhedra are given in table 1.

Let us note that the cube and the octahedron have the same number of edges, and that the number of faces of one is equal to the number of summits of the other one. The same is true for the dodecahedron and the icosahedron.

The generalized Euler relation is used in the case of other shapes, such as in foams or zeolithes [12].

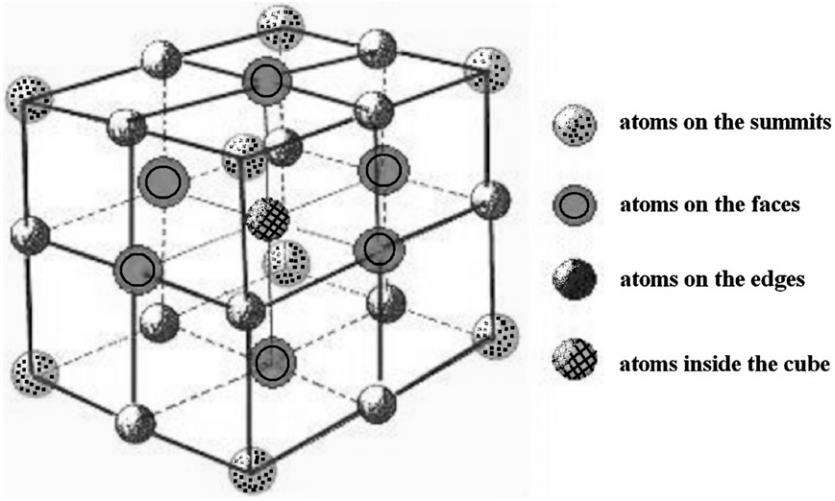


**Figure 2.** Cubic nanoparticule with atoms on the faces, the edges, the summits and inside.

**Table 1.** Number of faces (F), edges (A) and summits (S) for various geometric shapes.

| Geometrical shape | F | A | S |
|---|---|---|---|
| Tetrahedron | 4 | 6 | 4 |
| Cube | 6 | 12 | 8 |
| Octahedron | 8 | 12 | 6 |
| Dodecahedron | 12 | 30 | 20 |
| Icosahedron | 20 | 30 | 12 |

The Euler relation is useful when one studies the chemical reactivity of nanoparticles. Let us consider the case of cubic nanoparticles (figure 2). Let $N$ be the number of atoms on the edge of a cube. The total number of atoms on the summits of one cube, $S_o$, does not depend on the size of the cube: $S_o = S = 8$. The total number of atoms on the edges of one cube (excluding the atoms on the summits) is $A_r = A \cdot (N - 2) = 12 \cdot (N - 2)$. The total number of atoms on the faces of one cube (excluding the atoms on the summits and on the edges) is $F_r = F \cdot (N - 2)^2 = 6 \cdot (N - 2)^2$. The total number of atoms inside one cube is $I = (N - 2)^3$.

One easily verifies that the total number of atoms, $T$, is

$$T = S_o + A_r + F + I = N^3.$$

### *The chemical reactivity of nanoparticles*

It is well established experimentally that the chemical reactivity depends on the geometrical environment of the atoms. The reactivity of atoms on the summits, the edges or the faces are often different. This is due to the fact that the number of so-called dangling bonds are different. This implies that the reactivity of nanoparticles might depend on their size and shape.

Let $d_0$ be the diameter of one atom. One obtains

$$N \cdot d_0 = C/n.$$

In the following, it is assumed that $N \gg 2$.

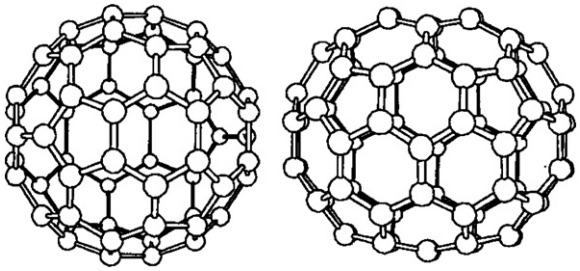

**Figure 3.** $C_{60}$ and $C_{70}$.

The total reaction rate on the summits is proportional to the number of summits in the powder:

$$S_{\text{tot}} = S/N^3 = 8/N^3 \propto n^3.$$

Similarly the total reaction rates on (for reactions taking place at) edges and faces are respectively proportional to

$$A_{\text{tot}} = A(N-2)/N^3 = 12(N-2)/N^3 \approx 12N^2/N^3 = 12/N \propto n^2$$
$$F_{\text{tot}} = F(N-2)^2/N^3 = 6(N-2)^2/N^3 \approx 6N^2/N^3 = 6/N \propto n.$$

It is then obvious that the reaction rates depend on both the shape (via $S$, $A$ and $F$) and the size (via $n$) of the nanoparticles. The reasoning is easily extended to other shapes.

It is one of the reasons why some materials appear to be chemically inert in the bulk state, while they are chemically active when nanopowders. For instance, it is well known that Au is chemically inert. However, it has been found that Au nanoparticles less than 3–5 nm in diameter are catalytically active for several chemical reactions, such as CO oxidation [9]. The variation of the catalytic activity with $n$ shows that the summits and to a lesser extent the edges contribute to this activity.

## Fullerenes

One of the most important molecules in the nanoscience field is the so-called buckminsterfullerene (or 'fullerene') molecule, also known as buckyball or $C_{60}$. Its shape is like a soccer ball (figure 3). Each carbon atom is bound to three other carbons in an alternative arrangement of pentagons and hexagons.

Fullerenes satisfy the Euler relation. Fullerenes are made of $H$ hexagons and $P$ pentagons. The numbers of faces, edges and summits satisfy

$$F = H + P \tag{3}$$
$$2A = 6H + 5P \tag{4}$$
$$3S = 6H + 5P. \tag{5}$$

The factor 2 in (4) comes from the fact that each edge is common to two polygons. Similarly, the factor 3 in (5) comes from the fact that a summit is common to three polygons. Given the Euler relation, a little algebra leads to

$$P = 12. \tag{6}$$

The value of $H$ depends on the value of $S$. In the case of $C_{60}$, $S = 60$, $H = 20$ and $F = 32$.

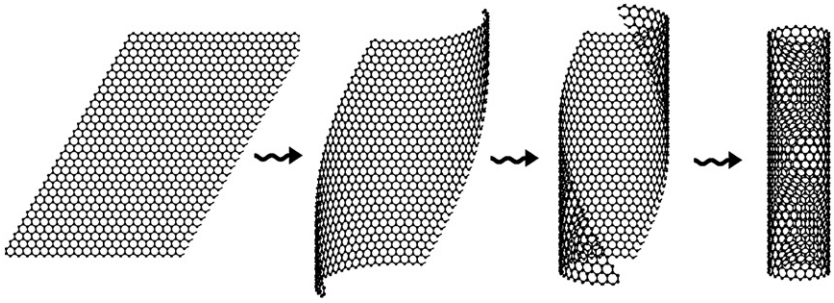

**Figure 4.** By rolling a graphene sheet back on itself, one forms a single-walled carbon nanotube.

Fullerenes with other values of $S$ are observed. For instance, $C_{70}$ is characterized by $S = 70$, $H = 25$ and $F = 37$.

It is worth noting that in $C_{60}$, the 60 atoms are geometrically equivalent. Every carbon is bound to three others. Moreover, every carbon atom is at the vertex of two hexagons and one pentagon. It is not in the case of $C_{70}$, in which atoms are divided into five categories. $C_{70}$ has the form of a rugby ball.

## Carbon nanotubes

Carbon nanotubes are another important material in NST. It is sometimes called the 21st century material, due to its particular physical properties. These are long cylindrical tubes, made of carbon. Each carbon nanotube is a single molecule. It may be thought of as a graphene sheet (from graphite) with its hexagonal structure rolled back on itself to form a cylinder (figure 4). The diameter of such single-walled nanotubes varies between 0.671 and 3 nm.

Three types of nanotubes are known, according to the way the graphene sheets are enrolled: arm-chair (figure 5(a), zigzag (b) and chiral (c)). One also observes multi-walled carbon nanotubes, made of coaxial single-walled nanotubes. Their diameter may attain 30–50 nm.

### *The specific area of carbon nanotubes*

Like other nanoparticles, the specific area of carbon nanotubes is large. In the graphene sheet, the interatomic distance is $d_{C\text{–}C} = 0.142$ nm. The area of one hexagon is $S_{hex} = 2.6 \times {d_{C\text{–}C}}^2 = 0.052$ (nm)$^2$. Every atom belongs to three different hexagons. Hence $S_{hex}$ corresponds to the area occupied by two atoms.

Given the fact that one mole of carbon weights 12 g, one easily calculates that 1 g of carbon nanotubes is characterized by an area of 1300 m$^2$.

### *Adsorption on carbon nanotubes*

Given their high specific area, carbon nanotubes are believed to be good candidates for hydrogen storage in future hydrogen tanks. Let us assume that one hydrogen atom may be adsorbed on each carbon atom [13]. One mole (1 g) of atomic hydrogen is adsorbed on one mole of carbon (12 g). One deduces that $1/12$ g of hydrogen is adsorbed by 1 g of carbon nanotubes, corresponding to an equivalent gas volume equal to 1.87 l H or 0.93 l $H_2$. This

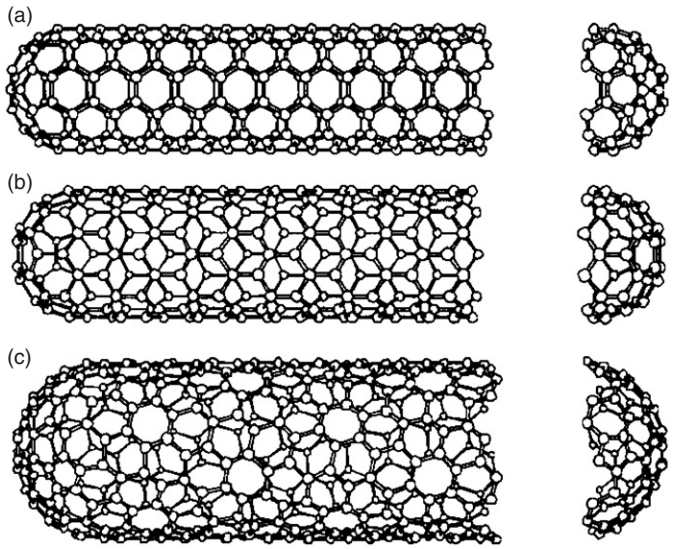


**Figure 5.** The three types of carbon nanotubes.

also means that the so-called maximum mass% hydrogen adsorbed on carbon nanotubes is equal to $1/(1 + 12) = 7.7\%$. In other words, storing 1 kg of hydrogen by adsorption on carbon nanotubes would require a tank weighing (at least) 13 kg.

### *Varia*

The fact that the specific area of carbon nanotubes is very high has a lot of potential applications. Among others, it is argued that carbon nanotubes attached to a surface would increase significantly the area of the plates of capacitors, hence allowing the design of ultracapacitors [14] and the storage of electrical energy. It is also argued that the carbon nanotubes might be major ingredients in adhesive systems (glues) where surface-to-surface contacts are important, such as gecko-like effects [15].

## Conclusions

Simple geometrical reasonings are shown to lead to the understanding of some of the particular properties of nanosystems. Size effects on the adsorption of gases and the chemical reactivity of nanosystems are explained.

## Acknowledgment

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