
Form and Matter: The Genesis of Materials

Prehistoric man discovered tools with polished and cut stone, the first steps in the use of natural resources. The history of humanity can be characterized by the nature of the objects used: ages of stone, bronze, iron, carbon (coal), silicon (or polymers), etc. Since then, technical advances have only increased and multiplied by developing the idea of substance and then matter associated with the progress of knowledge. In this context, a historical approach to the concept of materials is essentially linked to the development of the physical sciences since antiquity. Historians place their birth in Greece several centuries B.C. where it was only a part of knowledge grouped under the name “philosophy of nature” [ROS 79]. The associated classical image is that of the school of Athens with its two most famous representatives, Plato and Aristotle painted by Raphael (Figure 1.1). A simple approach relates the complementarity between shape and matter in the creation of an object. A typical example is that of a statue in which the sculptor imposes a particular form deemed ideal, with materials coming from different origins (marble, bronze, wood, etc.).

Since antiquity, this complementarity has persisted; this is what we will show in the initial part of this book. Therefore, we will pinpoint the key chronological events by distinguishing the different geometric forms involved and their evolution, independently of their content. The Renaissance in Europe is considered to be a fundamental period, followed by the establishment of the modern foundations of chemistry and physics from the 17th and 18th Centuries. Then, the creation of synthetic materials,

characteristic of contemporary chemistry, sparked their extraordinary evolution.

In the second part, we will show how these forms have become active surfaces or interfaces associated with a deeper description of matter always present in a limited volume. Thus, the notion of a finite system and of exchanges with the exterior becomes concrete when defining an object and its functionality. This approach is in fact a description and an analysis through the prism of our current knowledge where generalized thermodynamics will play an essential role.



Figure 1.1. Central part of Raphael's painting (c. 1520) entitled "the School of Athens" exhibited at the Vatican museum in Rome. Plato on the left points his finger to the sky while Aristotle on the right has his hands directed toward Earth: these gestures symbolize their respective philosophical approach of knowledge, rather idealist or even realistic. For a color version of the figure, see www.iste.co.uk/delhaes/materials.zip

1.1. Role and evolution of geometric shapes in chemistry

1.1.1. Shape and matter: the origins

When historians analyze the birth of Greek science, they recognize two main contributors. Following Thales, the school of Pythagoras developed

mathematics, in particular, geometry, and Empedocles proposed the existence of four primordial elements. In Athens, Plato adopted the system based on these four principles: fire, air, water and earth, associating a mathematical concept [BAU 04]. In the *Timaeus*, Plato proposed a geometric model where these elements are represented by regular polyhedra as shown in Figure 1.2. These five regular polyhedra consist of identical faces of variable numbers; triangular faces for the tetrahedron (fire), octahedron (air), icosahedron (water) and square (earth) but also pentagonal faces for the dodecahedron, representing the universe. In this context, we should mention the mechanistic approach of Democritus, who proposed the existence of a smaller piece of indivisible substance called a particle, a concept that we shall find much later with the existence of the atom.

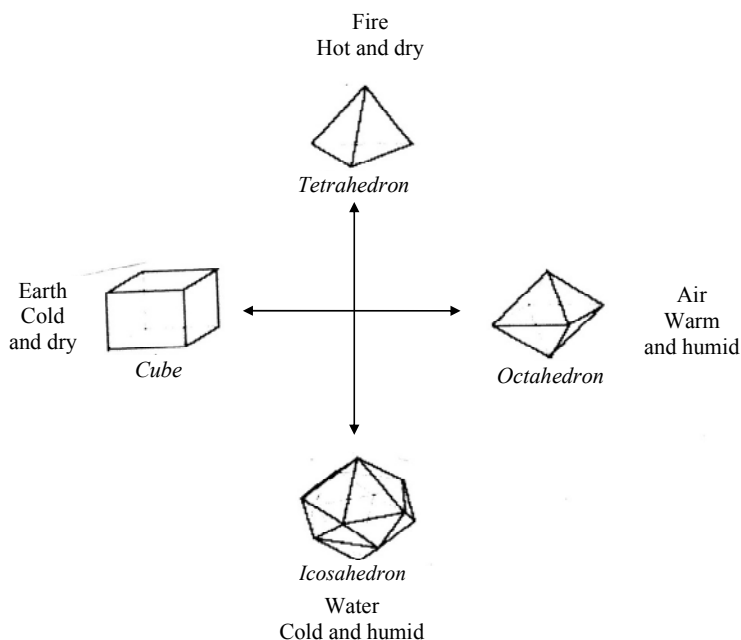


Figure 1.2. *The four primitive elements identified as Plato's regular polyhedra and associated with the qualities described by Aristotle (adapted from [LAU 01])*

The next step is due to “Aristotle’s *Physics*” that attributes great importance to the observation and development of a method of reasoning. It is a substantialist approach that attributes an essential role to the perceptive

qualities of man (the warmth, the cold, the wet, the dry). To change one element to another, one must act on a single quality or a couple of them [LAU 01], which is shown in Figure 1.2. Thus, Aristotle constructed a system by establishing a logic based on the symbiosis of shape and matter (called hylemorphism). Besides the results, establishing a scientific method through research into the causes is the main advantage. The exploration of materials mainly took place in Alexandria with the birth of Alchemy, which would be resumed and pursued by the Arab civilization. With regard to the gradual transition of natural substances to those isolated by laboratory methods, we can cite the eighth Century work by Gerber, who purified metals and various salts [BER 85].

1.1.2. From the Renaissance to modern chemistry

At the time of the Renaissance in Europe, toward the end of the 15th Century, the ideas of Plato and Aristotle were revived and idealized. Raphael's painting (Figure 1.1) symbolizes this appropriation. It shows Plato who seeks an ideal by raising his finger to the sky to suggest the notion of mathematical abstraction, and Aristotle who looks at the Earth and nature in general, sources of matter. Ideas of geometric space and perspectives will come through painting. They are associated with the rediscovery of the regular polyhedra drawn by Leonardo da Vinci in a work by Luca Pacioli ("De divina proportiona" published in Venice in 1509). Indeed, it was artist-engineers like Leonardo da Vinci or Albrecht Durer who brought a renewed interest at the scientific level. A significant example is an engraving called "Melancolia" where Durer drew symbols around the character, including a balance, an hourglass, a magic square, a sphere and an irregular polyhedron in which a face is reflected (see Figure 1.3). A little later Kepler embedded Plato's solids into a sphere, which is used as a model of the solar system ("Mysterium Cosmographicum" published in 1596).

The beginning of the 16th Century is also characterized by the revival of alchemical works that isolate pure bodies and medicine with the preparation of medicines: a typical approach is that of Paracelsus and his successors. The dominant fact is the birth of modern science toward the middle of the century and during the next century, reinforced by the rationalistic approach of Descartes. The creation and development of instruments for observation and measurement, especially in optics, have been decisive steps since the time of Aristotle.



Figure 1.3. *Copper engraving by Albrecht Durer (1513) famous for its elaborate composition showing a set of symbolic objects*

During the 18th Century, the importance of polyhedra was still significant. Theoretically, Euler established general geometrical relations to construct regular or semiregular polyhedra. Experimentally, the mineralogical contributions of various scientists, such as Haüy, a contemporary of Lavoisier, showed the presence of natural polyhedral crystals that appeared to be fundamental for geometrical crystallography (see the image presented in Figure 1.4). These polyhedra represent a concrete reality that will continue to develop.

From this revolution, modern chemistry was gradually born through the establishment of a nomenclature and new symbols to classify matter [LAU 01]. Many steps had to be taken over two centuries; these are described in the chapter on chemistry in the third volume of the encyclopedia of Sciences, Arts and Crafts edited by Le Rond d'Alembert and Diderot in 1780. The birth of chemical elements was initiated by Lavoisier followed by an advance in the structure of matter associated with the definition of a chemical system, proposed later by Dalton. The concept of an atom and then

of a molecule, going back to the idea of Democritus, was debated throughout the 19th Century: it was formalized with the establishment of the periodic classification of elements by Mendeleev in 1879 [ROS 79]. Let us conclude by indicating that the 19th Century was characterized by the study of chemical transformations and the creation of synthetic products, especially in organic chemistry. Its extension to the living domain with the birth of biochemistry and the establishment of a generalized chemical language were the main achievements.

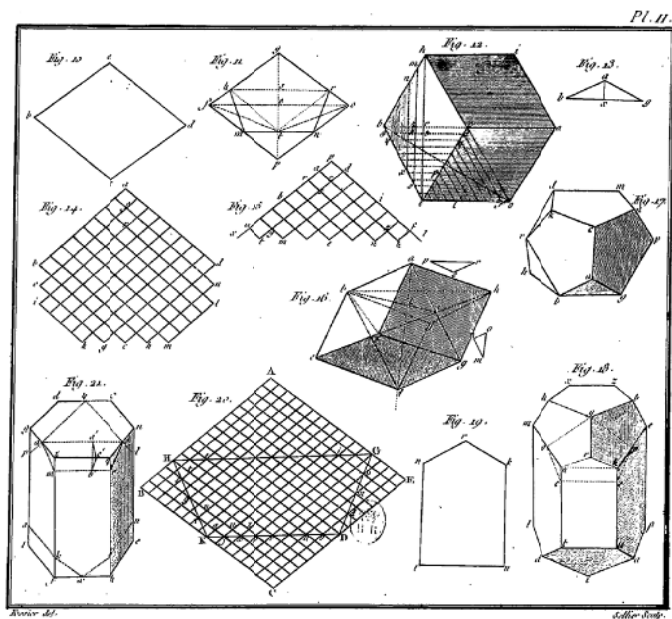


Figure 1.4. Example of an image showing various polyhedrons drawn by Haüy. "Essay on a theory of the structure of crystals applied to several kinds of crystallized substances" (editors Gogu  and W e de la Rochelle, Paris 1784)

1.1.3. Modern era

The beginning of the 20th Century was characterized by an in-depth study of the constitution of matter at the microscopic level because of two essential discoveries: X-ray diffraction and observations with electron microscopy [GUI 80]. It was around 1912–1915 that Le Von Laue and Bragg, father and son, discovered the method of diffraction of an electromagnetic wave allowing the reconstruction of the atomic structure of

crystallized solids. Then in the 1930s, Siemens engineers in Germany designed microscopes to visualize the texture of these solids, followed by scanning electron microscopy and then electron diffraction microscopy. Various instruments have been developed to produce high-resolution microscopes that are able to “see” the atoms. In this technological context, the discovery of near-field microscopes was made during the 1980s, allowing a more topographical description, that is to say, the visualization of surfaces. Even more recently, the development of fluorescence optical microscopes has led to significant advances in biology. Thus, these observation techniques are derived from the matter–radiation interaction and depend on the depth of penetration of the matter by the electromagnetic wave involved. They allow characterizations at several scales schematically from the micron to nanometer scale and are qualified as textural and structural, respectively.

These technical advances throughout the 20th Century have led to the return of geometric forms in chemistry both atomically and molecularly. The seven crystallographic structures listed are often the images of regular forms observed in mineralogy (see Figure 1.4). They obey particular rules, essentially the conditions of translation invariance and symmetry operations that define these crystal lattices. In particular, they exclude axes of symmetry of orders 5 or 7 in a plane, which do not lead to a complete filling of the Euclidean space. Work on non-crystallized solids such as glass has led to changes in these concepts. We must first mention the discovery of quasi-crystals in which a symmetry axis of order 5 is present: the local structure is a pentagon that does not lead to satisfactory planar tiling. This situation is to be compared to the theoretical tiling of Penrose but it is possible to form a two-dimensional network by bending the plane that eliminates possible hindrances. Indeed, 12 pentagons are combined in a sphere giving a dodecahedron. In this way, we find the last regular polyhedron identified by the Greeks, which can form a topological space that is curved rather than Euclidian, as proposed by Poincaré at the beginning of the 20th Century. By bending the space, the regularity of the crystal structures is seen despite appearing disordered, as in the case of glass [SAD 92].

At the level of the molecular structure, stable aggregates and cage-shaped solids can be also obtained by forming more elaborate polyhedra. Figure 1.5 shows two recent examples of monoatomic assemblies, composed of carbon and silicon, respectively. The discovery of fullerene in 1985, a molecule comprising 60 carbon atoms, was an epistemological breakthrough in

chemistry. This molecule is an icosahedron, a semiregular polyhedron known since Archimedes and described by Pacioli. It is the best understood molecule of this family, which consists of closed cages with a variable number of carbon atoms. With regard to silicon, we also see in Figure 1.5, a stable assembly of 33 atoms, which is a particular example of an aggregate. Variable polyhedral cages exist by forming clathrate-like phases. These situations show the extent of the polymorphism observed for different solids [DEL 11a].

An extension of these simple examples involves porous three-dimensional structures: these are zeolites of natural or synthetic origin [FER 07]. A historical example is shown in Figure 1.6 by presenting the atomic structure of Stilbite, a zeolite that is found in its natural state. This figure shows the presence of atomic tetrahedra, which play a fundamental role in modern chemistry. At present, a large number of alveolar solids have been synthesized by manipulating their architecture, size and geometry of the channels and access windows. This geometric parameter makes it possible to control their porosity, an essential parameter in surface chemistry.

Ultimately, these examples show how structural techniques have contributed to the better understanding of atomic and molecular structures, which are often constructed from polyhedra introduced by Greek philosophers (see Figure 1.2). In doing so, we have gone from a macroscopic description to a microscopic analysis of matter thanks to technological improvements, leading to a gradual reduction in the observation scale.

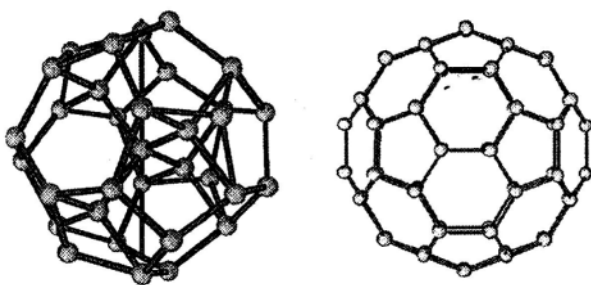


Figure 1.5. Examples of cage structures: on the right, fullerene C_{60} formed of pentagons isolated by hexagons, and on the left, a silicon aggregate consisting of a polyhedron with 28 atoms and a tetrahedron Si_5 inside

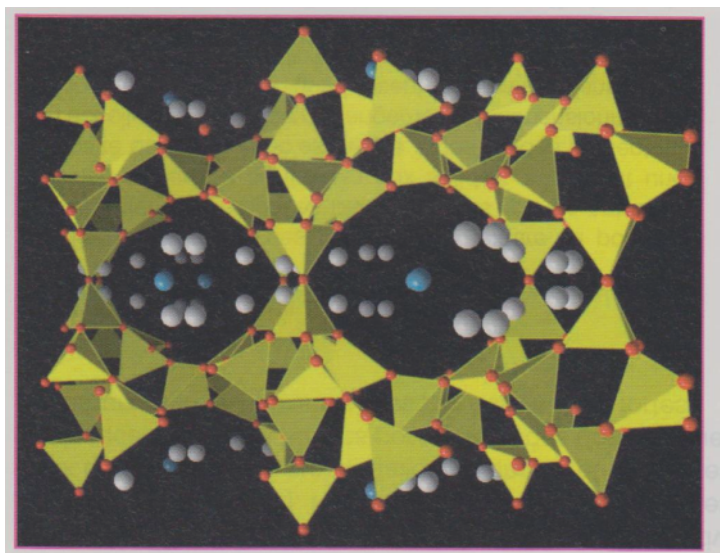


Figure 1.6. Structure of Stilbite, the first porous solid discovered in the 18th Century; the skeleton is formed by the combination of silicate and aluminate tetrahedra generating tunnels in which sodium (gray) and calcium (blue) ions are found (according to [FER 07])

1.2. Contributions of complexity of forms and thermodynamics

1.2.1. Development of more complex forms

The emergence of geometric forms more complicated than those of polyhedra led to the description of inert assemblies being extended to living environments. The founding works are attributed to D'Arcy Thomson in his book "On growth and form" published in Cambridge in 1917. It developed this field of research toward morphogenesis and the study of the mechanisms of formation of condensed matter. In this part, although we are interested in the inert matter observed under different conditions, the transition to a living environment is a critical aspect, which has initiated many studies. Thus, in an evolutionary medium subjected to exchanges, the appearance of more and more complex forms is observed. Various growths then occur at the atomic or molecular scale, defined as crystallogenesis but also at higher scales known as mesoscopic or macroscopic by morphogenesis. The purpose of understanding the formation and stability of these forms in the living world is to exploit them by biomimicry to create shapes, and ultimately, related

functions. A well-known example is the creation of chemical gardens following work initiated by Leduc (“The Physical Basis of Life and Biogenesis”, Masson, Paris 1906), which attempted to recreate mineral growths resembling living organisms by means of an osmotic effect [EAS 09]. This approach based on the self-formation of organized sets and generation of controlled chemical forms has recently been reviewed [BAR 15]. An example of macroscopic concretions confined between two plates is shown in Figure 1.7.

Systematic kinetic studies have been undertaken to analyze the forms obtained [COL 08]. A significant example is shown in Figure 1.8 where different types of crystallization of calcium carbonate are obtained according to varying experimental conditions. These mesocrystals result from different kinetics to the formation of polyhedra due to the involvement of weak chemical interactions. Thus, various forms are obtained by self-organization: they are analogous with biominerals, suggesting the idea of a continuous process.



Figure 1.7. Variety of chemical garden obtained by the addition of cobalt, copper, iron, nickel and zinc salts in a solution of sodium silicate (according to Barge et al. [BAR 15])

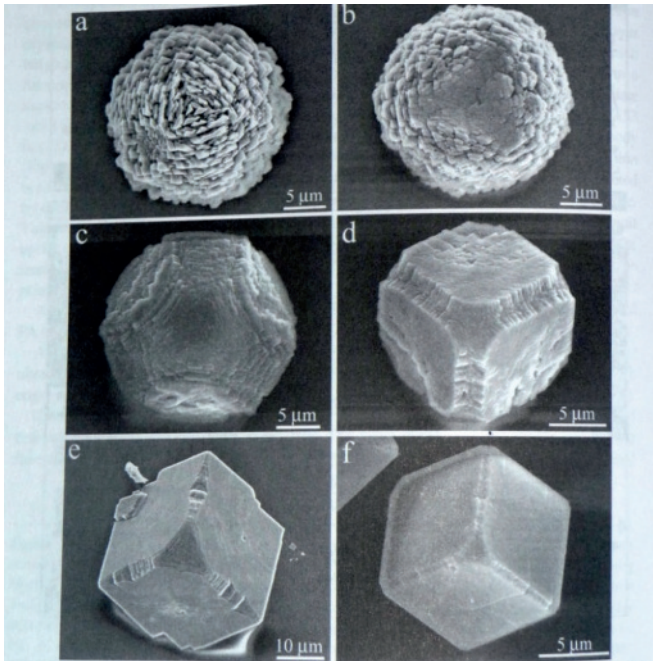


Figure 1.8. Photographs of calcium carbonate crystals precipitated from an aqueous solution containing a constant molar ratio of calcium and sulfur and with variable concentrations decreasing from plate (a) to (f) (according to [COL 08])

Recent studies confirm that, under the influence of a variable environment over time, different growth regimes exist and “floral” hierarchical structures are obtained and controlled [NOO 13]. Finally, the geometric extension to living forms considering developmental biology and involving morphogenesis cell mechanisms has been recently developed [PRO 08]. Particular examples include leopard spots, zebra stripes or even the formation of polygons in giraffes’ skin, resembling Penrose tiling. This point will be discussed in Chapter 2 describing the morphogenesis of materials, then in Chapter 9 for living systems.

1.2.2. Introduction to generalized thermodynamics

As we have just discussed, the emergence of evolutionary forms has been the subject of a large number of studies over the last century. Two main groups are represented by either a thermodynamic [GLA 73] or a

mechanistic [THO 72] approach. To illustrate this, we have shown in Figure 1.9 the covers of two books typical of these approaches and published almost simultaneously around 1970. For Thom [THO 72], it is a dynamic analysis of spatial structures and their transition from the catastrophe theory, which is considered as a neo-Platonic topological description on the geometry of shapes. On the contrary, for Glansdorff and Prigogine [GLA 71], the generalization of the concept of thermodynamic systems far from a state of equilibrium is fundamental. The stability or otherwise of the system depends on the nature, intensity and control of its exchanges or flows with the exterior, starting with the energy. Indeed, the significant contribution made over the past century has been the extension of the bases of phenomenological thermodynamics to situations outside an equilibrium state in a finite system interacting with its environment. The classic concepts of an isolated system and associated state functions and then their generalization for concrete situations in the presence of exchanges will be presented in Chapter 2.

Thus, these two schools of thought have existed since antiquity; the second more abstract one is centered on the mathematical description of dynamic phenomena that are often unstable, whereas the first one is more materialistic and directed toward modeling energy in a given situation. This is the second approach that we will develop.



Figure 1.9. Covers of books, published simultaneously after 1970, on the stability and evolution of dynamic systems: to the right that of Thom [THO 72] emphasizing the geometry of the forms, and to the left, written by Glansdorff and Prigogine [GLA 71], where thermodynamic fluctuations play an essential role

1.2.3. Toward a classification of materials

A generalist approach amounts to considering thermodynamics as the general basis for the study of materials. Therefore, they are like finite systems in interaction with their environment. The creation of an object for a specific use will depend not only on the intrinsic volumetric properties but also on the forms and characteristics of the interface. The nature of energy and/or mass exchanges will determine the field of application and a material can be defined by the physicochemical functionality of its surface or interface. This purpose leads to the existence of various classes of increasingly sophisticated materials that have followed the evolution of science and technology over the centuries.

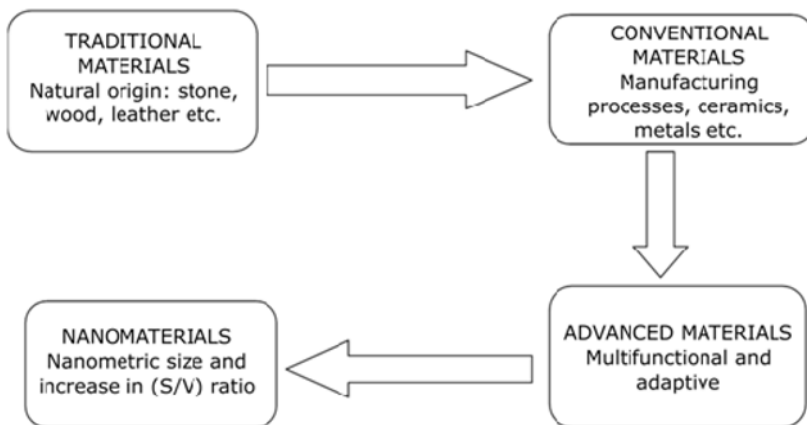


Figure 1.10. *Chronological approach to the evolution of materials*

A diagrammatic representation of the evolution of the main classes of materials is presented in Figure 1.10: it shows the major technological developments since early history with the birth of tools. In the absence of detailed knowledge of the substances, first natural and then synthetic, it is just an operational classification. This is the case for conventional materials, because modern chemistry has introduced several classes of conventional materials such as metals and their alloys or ceramics, or materials derived from organic synthesis, such as polymers or liquid crystals. Recently, so-called advanced materials have been created: they no longer provide a passive response to external fluctuations such as heat or mechanical stress, but they provide an active response to one or more interactions, fluctuations

or stimuli often of an electrical or optical nature. Known as functional or adaptive, they can transmit information and they are at the origin of more sophisticated multicomponent devices. The last stage of this evolution is that of nanomaterials, where the influence of surface functions will increase (the surface-to-volume or S/V ratio increases when size decreases). The nature and shape of the surface then become essential in these miniaturized devices.

1.3. Perspectives

The construction of an object requires some artistic creation when defining its shape whatever the type of material used. This is the case for a statue but also for a chair or a table to which a function must be associated, enforcing feet for the example cited. In the current context, this aesthetic component, which is always present, is called design. However, it is the transition from the aesthetic object to the technical object as an artifact that marks the boundary [SIM 58]. It is becoming more and more evident for highly technologically complex objects to be associated with ever more elaborate tools. This shape complexity will be extended by increasingly sophisticated functions. At the outset, this object has bulk properties that are described in physics (of the typical solid) as a thermodynamic system close to equilibrium. They will be exploited through energy transfers or exchanges to intelligently communicate with the environment. It is the nature of its separation surface with an appropriate shape and selectivity obtained by suitable treatments that will make it possible to define the materials and classify them as thermodynamic systems with a specific response. Prior to this, we will review the main achievements of phenomenological thermodynamics, the basis of this analysis.