1 Evolution of materials science and engineering: from natural to bioinspired materials

1.1 Early developments

For one brief moment, as one of us (MAM) walked into one of the fabled rooms of the British Museum, he was handed a tool used by early hominids two million years ago. The stone had a barely recognizable sharp edge but possessed a roundish side that fit snugly into the hand. It could have been used to cut through meat, scrape a skin, or crack a skull (Fig. 1.1). It was a brief but emotional event until the zealous anthropologist removed it from the hand that eagerly clasped the artifact and imagined himself deep in the Olduvai Gorge, slicing through the hide of a gazelle that had been hunted down by the group. This connection is at the heart of this book.

The first materials were natural and biological: stone, bones, antler, wood, skins. Figure 1.2(a) shows an Ashby plot of strength vs. density, for early neolithic materials. These natural materials gradually gave way to synthetic ones as humans learned to produce ceramics, then glass and metals. Some of the early ceramics, glasses, and metals are also shown in the plot, and they provide added strength. These synthetic materials expanded the range of choices and significantly improved the performance of tools. The long evolution of materials, from the stone shown in Fig. 1.1 to the cornucopia of materials developed in the past century, is shown in Fig. 1.2(b). Contemporary materials are of great complexity and variety, and they represent the proud accomplishment of ten thousand years of creative effort and technological development.

Why, then, this resurgence of interest in natural (or biological) materials, if synthetic materials have, as clearly shown in Fig. 1.2(b), a much superior performance? We have used our ingenuity to the maximum, but one way to overcome this is to look to nature for new designs and concepts. The materials that nature has at its disposal are rather weak (as will be shown in Chapter 2), but they are combined in a very ingenious way to produce tough components and robust designs. The central idea in biomimetics is to produce materials using our advanced technology along with bioinspired designs that have evolved in nature for millions of years. It is difficult, almost impossible, to reproduce all the steps in biological materials, which involve cellular processes. The complexity of a single cell is dauntingly beyond our capability. We therefore study nature, its designs and solutions, and derive principles that we can apply to modern materials. This is one of the important purposes of this book.

Figure 1.1.

One of the earliest tools, a chopper ~2 million years old, from the Olduvai Gorge; British Museum. (Used with permission; © The Trustees of the British Museum.)

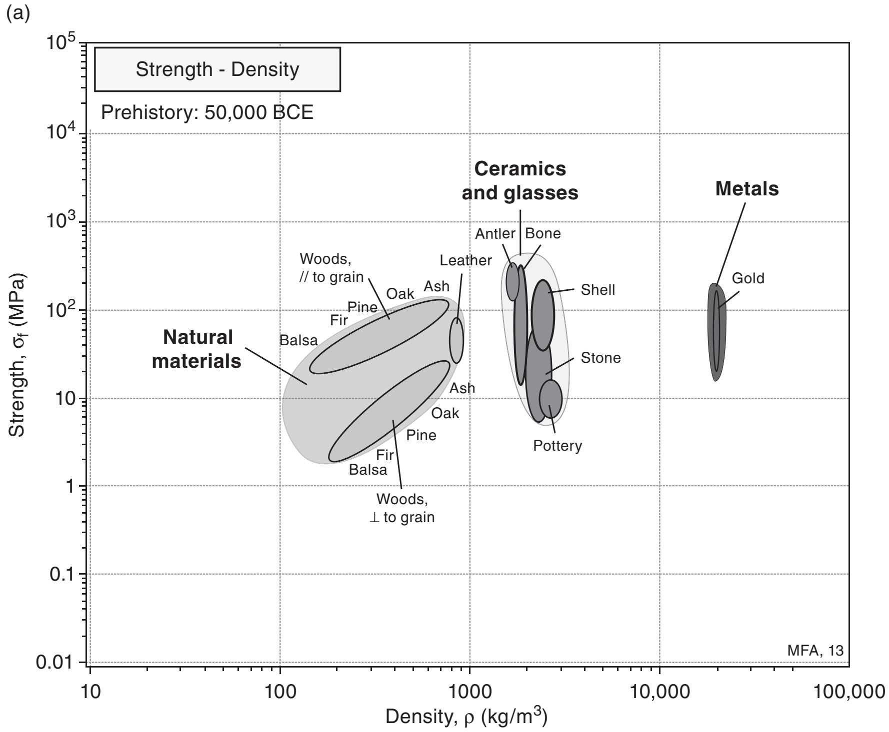

Figure 1.2.

Strength vs. density Ashby plots. (a) Prehistoric synthetic materials; (b) contemporary synthetic materials. (Figures courtesy of Professor Michael F. Ashby, Cambridge University.)

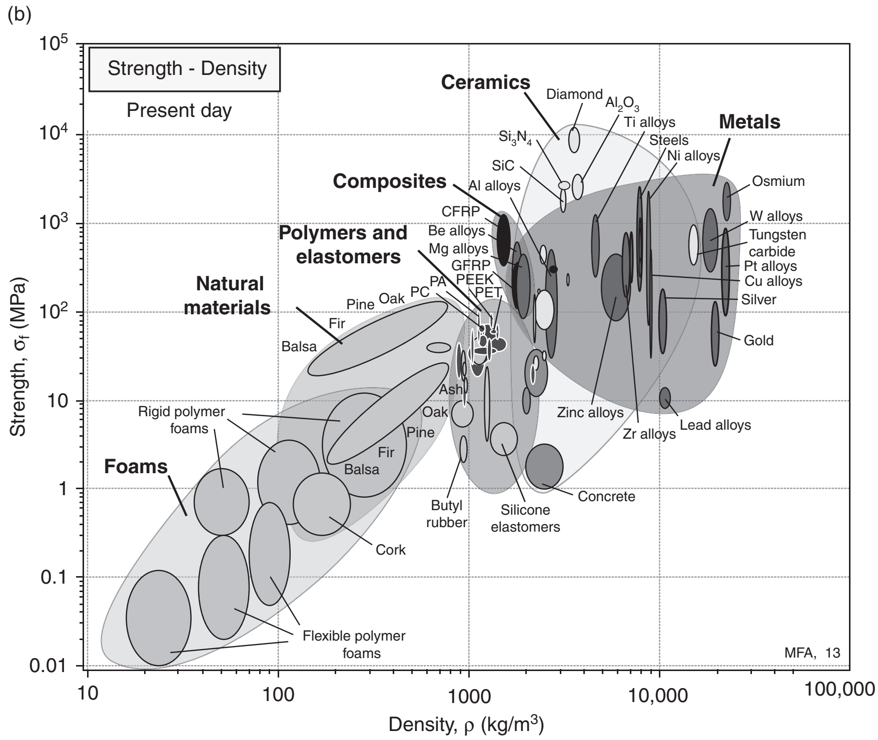

Figure 1.2. (cont.)

A brief historical overview shows how metallurgy gave rise to materials science and engineering, which expanded from primarily structural materials to functional and nanostructured materials starting in the 1970s, leading now to biological materials that serve as inspiration for complex hierarchical systems of the future.

1.2 Evolution of materials science and engineering

We can divide the evolution of materials science and engineering into three distinct phases.

1.2.1 Traditional metallurgy

Practiced over 5000 years and which dominated the field up to the first part of the twentieth century, traditional metallurgy can be represented by the metallurgical triangle (Fig. 1.3), which has extraction as the top vertex, with processing and properties as complementary components.

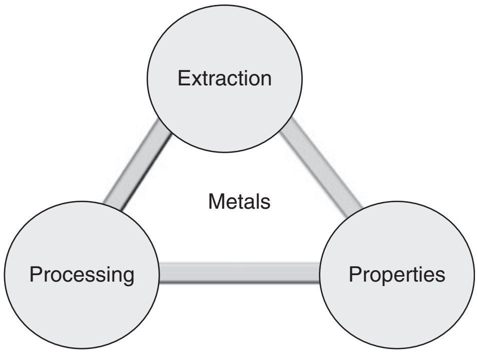

Figure 1.3.

Metallurgical triangle; traditional technology of past centuries.

The extraction of metals from ores represents a breakthrough in the civilizatory process. One of the oldest known archeological sites which shows evidence of mining is the "Lion Cave" in Swaziland. At this site, which is about 43 000 years old, paleolithic humans mined hematite, a reddish iron oxide (Fe_2O_3) and ground it to produce the red pigment ochre. Mines of a similar age in Hungary are believed to be sites where Neanderthals may have extracted flint for weapons and tools. The Egyptians also had large gold mining operations in Nubia.

Native copper, silver, and gold were certainly the first metals utilized. Their inherent ductility was a feature that was very attractive. The first vestiges of industrial-scale production of copper artifacts come from the Early Iron Age, 2700 BCE, from Jordan (Ben-Yosef *et al*., 2010; Levy, Najjar, and Higham, 2010). The excavations reveal a layout that in many aspects predates modern industrial production by many centuries. From these humble beginnings, the synthesis and processing of materials often defined civilization, and the bronze, iron, and silicon eras are closely connected with the emergence of new materials. A team led by Professor Thomas Levy (UC San Diego) and Dr. Mohammad Najjar (Jordan's Friends of Archaeology) (Levy *et al*., 2010), excavated an ancient copper-production center at Khirbat en-Nahas down to virgin soil, through more than 20 feet of industrial smelting debris, or slag. The factory had collapsed during an earthquake in about 2700 BCE. Buried in the rubble were hundreds of casting molds for copper axes, pins, chisels, bars, anvils, crucibles, along with metal objects and pieces of ancient metallurgical debris. Maps trace the copper production through about 70 rooms, alleyways, and courtyards. "This shows that the production of metal objects at Khirbat Hamra Ifdan was a highly specialized process performed by skilled crafts people," said Levy. The authors emphasize that the evidence of mass production found in the digs shows sophistication in mining, smelting, and fuel utilization, and demonstrates that Early Bronze Age leaders were able to plan, organize, and manage a large and technically skilled work force and train it to utilize complex technology. Analysis of the copper objects made at the ancient factory suggests that there was quality control at the factory.

A second dig discovered new artifacts, placing the bulk of industrial-scale production at Khirbat en-Nahas in the tenth century BCE, in line with the biblical narrative on the legendary rule of Kings David and Solomon. The research also documents a spike in metallurgical activity at the site during the ninth century BCE, which may also support the history of the Edomites as related by the Bible. Khirbat en-Nahas, which means "ruins of copper" in Arabic, is in the lowlands of a desolate, arid region south of the Dead Sea in what was once Edom and is today Jordan's Faynan district. The Hebrew Bible (or Old Testament) identifies the area with the Kingdom of Edom, foe of ancient Israel. Could these be King Solomon's fabled mines?

Box 1.1 Biomaterials

Biomaterials are as ancient as civilization, and there are reports of Egyptian mummies containing them. In modern times, the revolution brought on by Dr. J. Lister (in the 1860s), aseptic conditions of surgery, and the discovery of new materials propitiated this field, which is still expanding through innovation and the development of new procedures and devices.

Biomaterials may be classified in terms of the tissue response as follows.

- Biotolerant (e.g. stainless steel and polymethyl-methacrylate) materials release substances in non-toxic concentrations, which may lead to the formation of a fibrous connective tissue capsule.
- Bioinert (e.g. alumina and zirconia) materials exhibit minimal chemical interactions with adjacent tissue; a fibrous capsule may form around bioinert materials.
- Bioactive materials (e.g. tricalcium phosphate and Bioglass®) bond to bone tissue through bridges of calcium and phosphorus. However, the chemical bond between non-coated titanium implants and living tissue occurs through weak van der Waals and hydrogen bonds.

The structural classification of biomaterials follows the traditional lines of metals, polymers, ceramics, and composites. More complex arrays are usually called devices. Among metals, gold has been used as a biomaterial and is bioinert. Stainless steel (18wt.%Cr, 8wt.%Ni and 18–8 with Mo additions) fracture plates and screws led the way. Later, the composition (19wt.%Cr, 9wt.%Cr–Fe) became very successful. There are special stainless steel designations for bioimplant applications. For instance, the carbon level has to be very low to avoid embrittlement. This designation is called LC. For example, 304SSLC. In past years, titanium and titanium alloys, cobalt-based alloys (Vitallium), and an alloy exhibiting shape memory and super-elasticity effects, NITINOL (~50% Ti, ~50% Al), have found considerable applications. There is intense research activity in bioresorbable magnesium alloys. Implants made of these alloys dissolve at a prescribed rate so that second surgery for removal of the implant is not necessary. Magnesium is not toxic to the body.

Polymers found use as vascular implants, and a major breakthrough is the introduction of cloth prostheses made with Vinyon (a polyvinyl chloride and polyacrylonitide copolymer), Orlon, Dacron, and Teflon porous fabric that have enabled the formation of a neointima layer covering the inside wall of the implant, thus preventing blood coagulation. Polyethylene (both low density and high density) is used in many applications (e.g. lumens). It should be noted that the difference in density between LDPE and HDPE is minimal; however, the differences in mechanical response are

Box 1.1 (cont.)

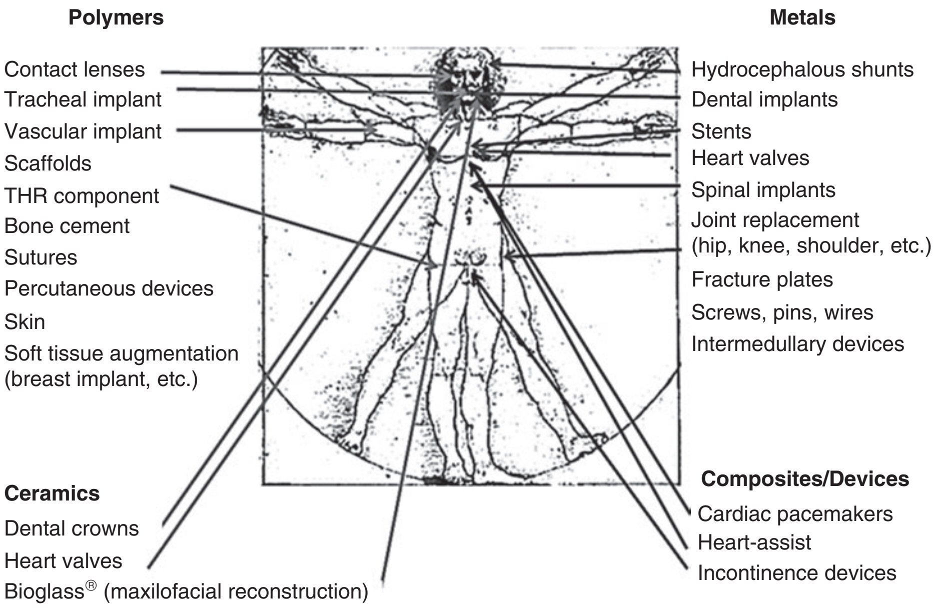

Figure B1.1.

Leonardo's Vitruvian Man and four classes of biomaterials.

striking, HDPE being a much more compact and organized structure with a higher yield stress and lower ductility. In the area of tissue engineering, biodegradable polymers have found great application and have led the way in the formation of scaffolds on which cells and tissue can grow, as they are reabsorbed by the body. Both biopolymers and synthetic polymers are used (Sonntag, Reinders, and Kretzer, 2012).

Ceramics have also found applications, primarily in dental reconstruction but also in scaffolds for bone (e.g. coral) and in total hip replacements because of the low wear rate.

Figure B1.1 shows selected applications of biomaterials in the human body in an illustrative manner.

1.2.2 The structure–properties–performance triangle

Created by Morris Cohen (Cohen, Kear, and Mehrabian, 1980) in the 1970s, the structure–properties–performance triangle emphasizes the connection between these three elements and presents MSE in a new light, with a novel approach unique to it. The unified approach to the study and utilization of metals, ceramics, polymers, and their composites as pioneered by M. Fine (see e.g. Fine and Marcus (1994)) comprises the second stage of evolution of MSE.

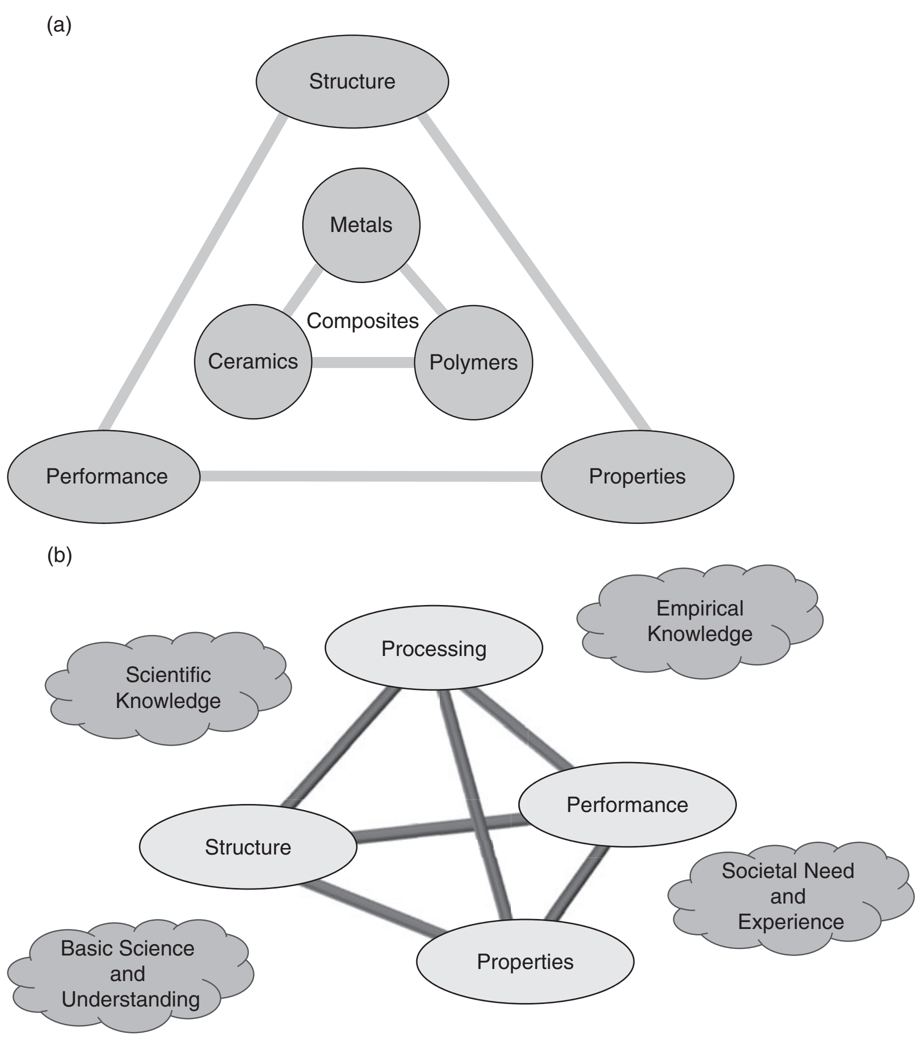

Figure 1.4.

The materials science and engineering revolution: a unified approach to metals, ceramics, and polymers. (a) The original Cohen structure–properties–performance triangle; (b) a modernized version.

The elements of the unified materials approach are shown in Fig. 1.4(a) in their original rendition (Cohen *et al.*, 1980). A more contemporary version of this schematic is shown in Fig. 1.4(b). This structure–property paradigm is still at the heart of MSE research.

1.2.3 Functional materials

In the 1990s, the tetrahedron proposed by G. Thomas, and which forms the cover of *Acta Materialia* (Fig. 1.5), emphasized the growing importance of functional materials, a

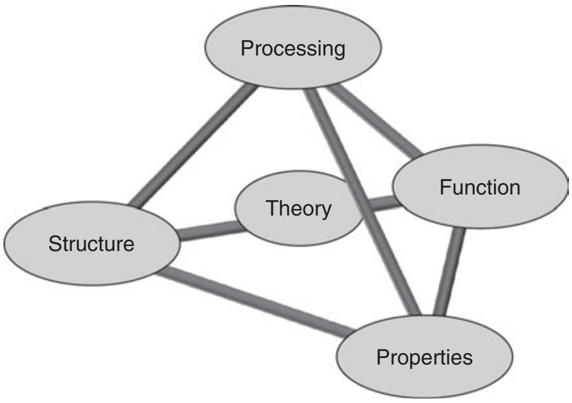

Figure 1.5.

The materials science and engineering (*Acta Materialia*) tetrahedron.

departure from the earlier focus in structural materials. What we denominate "functional" materials are electronic, magnetic, and optical properties.

1.3 Biological and bioinspired materials

The new field of biological and bioinspired materials, which is the theme of this book, is well represented by the *heptahedron* (Fig. 1.6), which contains features that are unique to natural materials and that we hope to incorporate, through biomimetics, into synthetic systems. It is based on the biological materials pentahedron created by Arzt (2006), expanded to incorporate essential elements. The heptahedron is indicative of the complex contributions and interactions necessary to understand fully and exploit (through biomimicking) biological systems. Biological materials and structures have unique characteristics that distinguish them from synthetic counterparts. Evolution, environmental constraints, and the limited availability of materials dictate the morphology and properties. The principal elements available are oxygen, nitrogen, hydrogen, calcium, phosphorous, and carbon. The most useful synthetic metals (iron, aluminum, copper) are virtually absent – only present in minute quantities and highly specialized applications. The processing of these elements requires high temperatures not available in natural organisms. The seven components are:

- *Self-assembly* – in contrast to many synthetic processes to produce materials, the structures are assembled from the bottom up, rather than from the top down. This is a necessity of the growth process, since there is no availability of an overriding scaffold. This characteristic is called "self-assembly."
- *Self-healing capability* – whereas synthetic materials undergo damage and failure in an irreversible manner, biological materials often have the capability, due to the

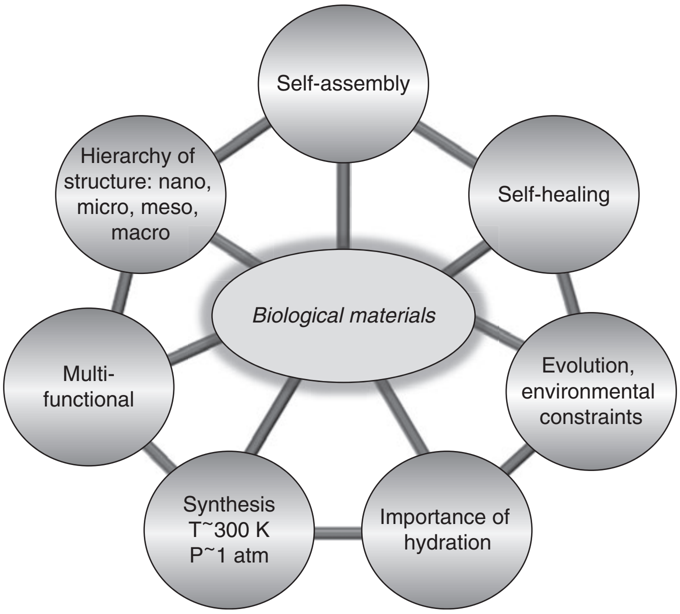

Figure 1.6.

Fundamental and unique components of biological materials. (Heptahedron inspired by Arzt (2006).)

vascularity and cells embedded in the structure, to reverse the effects of damage by healing.

- *Evolution and environmental constraints* – the limited availability of useful elements dictates the morphology and resultant properties. The structures are not necessarily optimized for all properties, but are the result of an evolutionary process leading to satisfactory and, importantly, robust solutions.
- *Hydration* – the properties are highly dependent on the level of water in the structure. Dried skin (leather) has mechanical properties radically different from live skin. There are some remarkable exceptions, such as enamel, but this rule applies to most biological materials and is of primary importance.
- *Mild synthesis conditions* – the majority of biological materials are fabricated at ambient temperature and pressure and in an aqueous environment, a significant difference from synthetic materials fabrication.
- *Functionality* – many components serve more than one purpose; for example, feathers provide flight capability, camouflage, and insulation; bones are a structural framework, promote the growth of red blood cells, and provide protection to the internal organs; the skin protects the organism and regulates the temperature. Thus, the structures are called "multifunctional."
- *Hierarchy* – there are different, organized scale levels (nano- to macro-scale) that confer distinct and translatable properties from one level to the next. We are starting

to develop a systematic and quantitative understanding of this hierarchy by distinguishing the characteristic levels, developing constitutive descriptions of each level, and linking them through appropriate and physically based equations, enabling a full predictive understanding.

The study of biological systems as structures dates back to the early parts of the twentieth century. The classic work by D'Arcy W. Thompson (Thompson, 1968), first published in 1917, can be considered the first major work in this field. He looked at biological systems as engineering structures, and obtained relationships that described their form. In the 1970s, Currey investigated a broad variety of mineralized biological materials and authored the classic book *Bones: Structure and Mechanics* (Currey, 2002). Another work of significance is Vincent's *Structural Biomaterials* (Vincent, 1991). The field of biology has, of course, existed and evolved during this period, but the engineering and materials approaches have often been shunned by biologists.

Materials science and engineering is a young and vibrant discipline that has, since its inception in the 1950s, expanded into three directions: metals, polymers, and ceramics (and their mixtures, composites). Biological materials are being added to its interests, starting in the 1990s, and are indeed its new future.

Many biological systems have mechanical properties that are far beyond those that can be achieved using the same synthetic materials (Vincent, 1991; Srinivasan, Haritos, and Hedberg, 1991). This is a surprising fact, if we consider that the basic polymers and minerals used in natural systems are quite weak. This limited strength is a result of the ambient temperature and the aqueous environment processing, as well as of the limited availability of elements (primarily C, N, Ca, H, O, Si, P). Biological organisms produce composites that are organized in terms of composition and structure, containing both inorganic and organic components in complex structures. They are hierarchically organized at the nano-, micro-, and meso-levels. The emerging field of biological materials introduces numerous new opportunities for materials scientists to do what they do best: solve complex multidisciplinary scientific problems. A new definition of biological materials science is emerging; as presented in Fig. 1.7; it is situated at the confluence of chemistry, physics, and biology.

Biological systems have many distinguishing features, such as being the result of evolution and being multifunctional; however, evolution is not a consideration in synthetic materials, and multifunctionality still needs further research. Some of the main areas of research and activity in this field are:

- Biological materials: these are the materials and systems encountered in nature.
- Bioinspired (or biomimicked) materials: approaches to synthesizing materials inspired by biological systems.
- Biomaterials: these are materials (e.g. implants) specifically designed for optimum compatibility with biological systems.
- Functional biomaterials and devices.