


ADVANCES IN NANOMATERIALS AND APPLICATIONS

HISTORY OF NANOTECHNOLOGY

*From Prehistoric to
Modern Times*

Edited by

MADHURI SHARON

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History of Nanotechnology

Scrivener Publishing
100 Cummings Center, Suite 541J
Beverly, MA 01915-6106

Advances in Nanotechnology & Applications

Series Editor: Madhuri Sharon

The unique properties of nanomaterials encourage the belief that they can be applied in a wide range of fields, from medical applications to electronics, environmental sciences, information and communication, heavy industries like aerospace, refineries, automobile, consumer and sports good, etc.

This book series will focus on the properties and related applications of nanomaterials so as to have a clear fundamental picture as to why nanoparticles are being tried instead of traditional methods. Since nanotechnology is encompassing various fields of science, each book will focus on one topic and will detail the basics to advanced science for the benefit of all levels of researchers.

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From Pre-Historic to Modern Times

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This edition first published 2019 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA

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Library of Congress Cataloging-in-Publication Data

ISBN 978-1-119-46008-4

Cover image: Pixabay.Com

Cover design by Russell Richardson

Set in size of 13pt and Minion Pro by Exeter Premedia Services Private Ltd., Chennai, India

Printed in the USA

10 9 8 7 6 5 4 3 2 1

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Preface

Nanotechnology is a very rich field of science due to informational input by physicists, chemists, engineers, geologists and biologists. However, this book was written from a layman's perspective and questions whether it is a new science, or, like other sciences, was already discovered and utilized by nature. Did nature, which created an entire universe made up of galaxies, the solar system, the Earth and even living beings from the smallest known entities, also create nanoparticles? It is a difficult subject to write about since compiling knowledge about nature that has not been recorded in an easily decipherable form, coupled with the possibility of some natural records having been lost during the long periods of history either by nature or us, makes most information unavailable to us. We realized that apart from nature, human beings have also knowingly or unknowingly fabricated and utilized nanoparticles for various reasons. Looking back through history and searching for the existence of nanoparticles, not visible to the eye, and nanotechnology, not yet known to us but seen in nature, has been an interesting journey for us. I hope we have made it interesting enough for the readers also.

Madhuri Sharon
September 2018

Foreword



Dr. Neelam Koomar

It is a novel idea to write about nanotechnology in ancient periods. Since I have been a student of ancient Indian history and culture, it is difficult for me to review science, especially nanotechnology and its effect in ancient times.

Dr. Madhuri Sharon and her teammates have very effectively described this rich field of science applied in the past. They have very lucidly described its application in prehistoric times. In ancient India, unknowingly, people have used it in the field of medicine, cosmetics, metallurgy, etc. Nanotechnology flourished in the Maya civilization of South America and also in Roman culture.

If you sincerely analyze the Vedic period and Ramayana era, nanoparticles and nanotechnology were utilized.

Thanks to Dr. Madhuri Sharon who introduced me to nanotechnology a decade ago. I wish Dr. Sharon and her team great success.

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How Old is Nanotechnology?

Mrinal Chakre and Madhuri Sharon

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*I want to know why the universe exists, why there is something
greater than nothing.*

Stephen Hawking

Preamble

When we sat down to write this chapter, the first thing that came to mind was whether there are nanoparticles existing in nature which are not man-made or fabricated. Both biotic and abiotic natural nanoparticles came to mind. The next question was, “Since when?” Nanoparticles by definition are particles of any shape with an equivalent diameter of 1–100 nm, i.e., specifically those particles that are intermediate in size between bulk materials and atomic/molecular structures or quantum dots. These nano-size particles exhibit unique physical and chemical properties due to their distinctive novel properties related to a high surface area to volume ratio and/or quantum effects.

Table 1.1 Scales of Measurement.

Factor	Symbol	Prefix	Factor	Symbol	Prefix
10^{-18}	A	Atto	10^1	Da	Dekka
10^{-15}	F	Femto	10^2	H	Hector
10^{-12}	P	Pico	10^3	K	Kilo
10^{-9}	N	Nano	10^6	M	Mega
10^{-6}	μ	Micro	10^9	G	Giga
10^{-3}	M	Milli	10^{12}	T	Tera
10^{-2}	C	Centi	10^{15}	P	Peta
10^{-1}	D	Deci	10^{18}	E	Exa

A quick glance at various scales of measurement (Table 1.1) gives an idea of how small a nanometer is. A nanometer (nm) is one thousand-millionth of a meter. For comparison, a red blood cell is approximately 7,000 nm wide and a water molecule is almost 0.3 nm across. People are interested in the nanoscale (which is defined to be from 100 nm down to the size of atoms (approximately 0.2 nm) because it is at this scale that the properties of materials can be very different from those at a larger scale. Nanoscience is defined as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale; and nanotechnologies as the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nm scale.

Let us look at some of the known naturally occurring nanoparticles. Depending on the origin, a distinction is made between three types of nano-size particles: (i) natural, (ii) incidental and (iii) engineered. *Natural nanoparticles* from volcanic dust, lunar dust, mineral composites, etc., have existed since the beginning of the Earth. Some such nanoparticles still

occur in the environment and are termed *incidental nanoparticles*, also defined as waste or anthropogenic particles, which take place as the result of man-made industrial processes such as diesel exhaust, coal combustion, welding fumes, etc.

1.1 Introduction

Our present awareness of nanotechnology (materials of a size between 1–100 nm, having novel properties that are not found in their bulk counterpart) started in the 1980s, caused by the convergence of experimental advances such as the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985, with the elucidation of a conceptual framework for the goals of nanotechnology. Nanotechnology became popularized as a result of the Nobel Prize being awarded for many nanoparticle discoveries; i.e., Nobel Prizes were awarded to Heinrich Rohrer in 1986 for the invention of the scanning tunneling microscope, to Kroto *et al.*, in 1985 for the discovery of fullerene, and to Geim and Novoselov in 2010 for graphene. The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (Caltech) on December 29, 1959, long before the term nanotechnology was coined in 1974 by Taniguchi.

Our concern in this chapter is to address the questions of “How old is nanotechnology?” and “Are there naturally occurring nanoparticles; if so, since when?” To know the existence of nanoparticles on Earth, which is part of this universe, we realize that their origin plays a great role in the existence of any matter.

There was a time when scientists thought Earth was at the center of the universe. As late as the 1920s, we did not realize that our galaxy was just one of many in a vast universe. Only later did we recognize that the other galaxies were running

away from us—in every direction—at ever greater speeds. Our universe is both ancient and vast, and expanding out farther and faster every day. This accelerating universe, the dark energy that seems to be behind it and other puzzles, like the exact nature of the Big Bang and the early evolution of the universe, are among the great puzzles of cosmology.

About 11 to 15 billion years ago all of the matter and energy in the universe was concentrated into an area the size of an atom. At that moment, matter, energy, space and time did not exist. Then suddenly, the universe began to expand at an incredible rate and matter, energy, space and time came into being (the Big Bang). As the universe expanded, matter began to coalesce into gas clouds, and then stars and planets. Our solar system formed about 5 billion years ago when the universe was about 65% of its present size. Today, the universe continues to expand along with the existence of nanoparticles.

Though the chemical properties of a bulk material depend on its molecular structure, when they assemble at the nano level they exhibit other unique and novel physicochemical properties. That may be why nature decided to naturally synthesize particles at the nano level to contribute to the evolution of our Earth or perhaps other planets also.

Prehistoric events date back to the time before the invention of writing—roughly 5,000 years ago. Without access to written records, scientists investigating the lives of prehistoric people face special challenges. A lot of knowledge has been lost due to man-made activities like wars, as well as natural calamities such as earthquakes, tsunamis, floods, volcanic eruptions and meteor showers, which have caused tremendous adverse effects.

What are natural nanomaterials? As the name suggests, natural nanoparticles are synthesized by nature without the interference of man.

At a very vast level of understanding of naturally occurring nanoparticles, Sharma *et al.*, [1] have considered five

major points, namely, (i) the presence of naturally occurring nanoparticles in the atmosphere, hydrosphere, lithosphere and biosphere, (ii) the presence of naturally occurring organic matter and its role in the formation of metal nanoparticles like silver and gold, (iii) another important matter that they have considered is how the reaction between reactive oxygen species and natural organic matter at elevated temperature and/or exposure to light supports the formation of metal nanoparticles, (iv) how the properties and role of water especially related to the pH, redox conditions, ions/ionic strength and concentrations of natural organic matter determine the growth and stability of NPs in the aquatic environment, and finally (v) the impact of natural conjugation of organic matter with natural metal nanoparticles on toxicity, which may be less than that of the engineered nanoparticles that are surface-coated by polymers and/or surfactants.

These considerations are based on the fact that there are naturally occurring nanoparticles that came into existence even before the formation of Earth. In nature, nanoparticles are naturally formed in all spheres of the Earth (atmosphere, hydrosphere, lithosphere and biosphere), either by chemical, photochemical, mechanical, thermal, and biological processes separately or in combination; and/or also by extraterrestrial inputs. Typical naturally occurring nanoparticles include (a) metals such as Ag, Au and Fe, (b) metal oxides, e.g., Al_2O_3 , Fe_2O_3 , MnO_2 and SiO_2 , (c) metal sulfides like FeS_2 and ZnS , etc.

1.2 Nano-Geosystem for Abiotic Nanoparticles Formation

In the first stage of chemical evolution on earth, molecules formed in the primitive environment were simple organic substances such as amino acids. This concept was first proposed in 1936 by Oparin [2]. He considered hydrogen, ammonia,

water vapor and methane to be components present in the early reducing atmosphere. Oxygen was lacking in this chemically reducing environment. He stated that UV radiation from the Sun provided the energy for the transformation of these substances into organic molecules.

In the second stage of chemical evolution, the simple organic molecules, e.g., amino acids, formed, which eventually joined together, forming structures such as peptides, proteins, etc. Linking of smaller units (in the absence of enzymes provided by living systems) occurred by the process of dehydration to form polymers. These polymers or organic monomers by some process must have moved onto the fresh lava or hot rocks, which would have allowed polymers to form abiotically. To support this hypothesis, Fox and Harada [3] abiotically synthesized polypeptides.

The third step in chemical evolution suggests that polymers interacted with each other and organized into aggregates, known as protobionts. Protobionts are not capable of reproducing but have other properties of living things. In the final step of chemical evolution, the protobionts developed the ability to reproduce and pass genetic information from one generation to the next. Some scientists theorize that RNA was the original hereditary molecule. Gradually DNA replaced RNA as the genetic material.

“Do nanoparticles exist in nature?” and “If so, since when?” are million-dollar questions!!! The answer to the first question is YES, almost every chemical formed (except liquids and gases) has some sort of structure on the nanometer scale. Moreover, many such examples provided by nanogeoscience studies prove it. Another example worth mentioning regarding the existence of nanoparticles in Earth’s atmosphere is mentioned by Eather [4] and Savage [5]. They suggested that the northern sky bright lights near the polar region (known as aurora borealis, a term coined by Galileo Galilei), which appear in September, October, March and April, are optical

phenomena caused by the interactions between the ionosphere nanoparticles and solar wind particles under the influence of Earth's magnetic field.

In nature, the formation of nanoparticles occurs via processes like *weathering*, i.e., mechanical processes combined with dissolution/precipitation; *colloid formation* in rivers, and by *volcanic activity* that involves fast cooling of fumes and explosions expelling tephra.

In a nutshell, it is evident that nanoparticles are formed at phase boundaries, e.g., solid–gas wind erosion, liquid–gas evaporation of sea spray, solid–liquid weathering of rocks/minerals, etc. Such nanoparticles are produced in the form of colloids, aerosols, and dust (present as cosmic dust, constituents of soils and sediments, hydrothermal/chemical deposits, mineral nuclei). Chemical composition of these nanoparticles can be categorized as: Metal oxides/hydroxides, metals or alloys, non-metals such as carbon allotropes and others, silicates, sulfides of Cu and Zn containing pyrites FeS_2 and ZnS , and nanoframboids in high temperature black smoker hydrothermal vents, sulfates, halides, and carbonates. Moreover, natural Au particles have been observed in both low- and high-temperature locations during ore mining activities [6].

1.2.1 Nanoparticles Occurring in Mineral Composites

1.2.1.1 *Allophane and Smectites*

Allophane is an amorphous to poorly crystalline hydrous aluminium silicate clay mineral. Its chemical formula is Al_2O . According to Theng and Yuan [7], soil has complex ecosystems with diverse compositions which also include nanoparticles. Hochella *et al.*, [8] and Parfitt [9] supported this belief and suggested that due to either biotic or abiotic processes, all the minerals go through a nanophase stage during formation. Allophane is one of the typical examples of natural nanoparticles that only

exist in the nano-size range of <100 nm, which is ubiquitous in soil environments [10]. The ratio of Al/Si in allophane varies between 1 and 2. Allophane nanoparticles are spherical and hollow, with an outer diameter of 3.5–5.0 nm and a wall thickness of 0.7–1.0 nm [7]. However, Filimonova *et al.*, [11] recently showed that the spheres combine to form larger aggregates that can be up to 60–100 nm in diameter. These nanoparticles affect the physical and chemical properties of soil because of their large surface area, large number of surface functional groups per unit of mass and unique electrical or magnetic properties [12, 13]. It must be mentioned here that according to Chen *et al.*, [14], Eusterhues *et al.*, [15], Qafoku [16] and Sharma *et al.*, [1] the soil condition, such as soil pH, organic carbon content and dissolved organic matter concentration and other impurities, may affect the formation and phase transformation of natural nanoparticles.

1.2.1.2 Opal

Another well-known natural nanostructure is Opal, which consists of SiO_2 nanospheres of 150 to 300 nm diameter in a hexagonal or cubic close-packed lattice. Its pretty colors come from diffraction from regular arrays of these nanoparticles, so opal is also nature's photonic crystal. On the basis of SEM analysis, Gaillou *et al.*, [17] have reported on two common opals, i.e., Opal-AG and Opal-CT; both are built from nanograins that average ~ 25 nm in diameter (Figure 1.1).

In Opal-AG, nanograins are arranged into spheres that have successive concentric layers or in radial structures. The spheres are typically cemented by non-ordered nanograins. In Opal-CT, nanograins have different degrees of ordering, ranging from none (aggregation of individual nanograins), to an intermediate stage in which they form tablets or platelets, which form lepispheres. A *lepisphere* is a microcrystalline, blade-shaped crystal of a metastable variety of quartz, composed of cristobalite with interlayered lattices of tridymite,

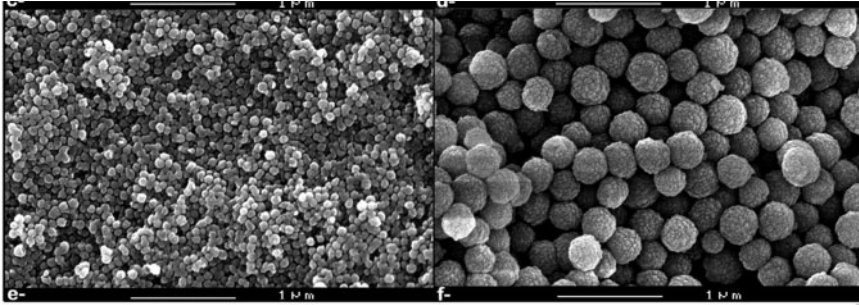


Figure 1.1 SEM images of common opal. (e) Fire opal-AG from Slovakia (Dubník, no. 637) consisting of spheres that are not ordered and are too small (~80 nm in diameter) to diffract light. (f) White opal-AG from Honduras with spheres ~ 280 nm in diameter (adequate for a red play-of-color), which do not show a regular arrangement. (Reproduced from [17])

aggregates of which often occur during the transformation of opal into quartz chert. Lepspheres are cemented by non-ordered nanograins.

1.2.2 Nanoparticles from Volcanic Activities

There are reports of the presence of nanoparticles expelled by volcanoes along with other material. According to Tepe and Bau [18], an example of a top-down production approach in nature is volcanic activity occurring at very high temperature. They have reported an array of metal nanoparticles of Fe, Ca, Hg, Al and Co; and also nanoparticles of Si and C. These nanoparticles were found during the geochemical study of glacier-fed rivers, glacial surface runoff, glacial base flow, and pure glacial meltwater from southern Iceland that had been sampled 25 days after the explosive eruptions at Eyjafjallajökull in 2010.

1.2.3 Nanoparticles from Dust of Cosmic Sources

Approximately 40,000 tones/year of cosmic dust enter the Earth's atmosphere. These dusts come from (i) the *interplanetary dust cloud* surrounding the Sun, (ii) *interplanetary dust* is present between Mars and Jupiter, (iii) *comets* or *meteorites*

entering the atmosphere, which disintegrate and accumulate as cosmic dust, and (iv) *inter-stellar dust* that originates from beyond our solar system [19].

Cosmic objects move in space at very high speed, sometimes over 150,000 km/h. When they approach the Earth, their speed slows down and due to the friction with the Earth's atmosphere the meteorites burn up and give their characteristic glow. The smaller particles produce friction that reduces their speed through the atmosphere, but they do not burn up and finally reach the surface of the Earth.

Using an infrared (IR) detection technique, the interplanetary dust composition and size were measured during space missions like Pioneer 10 (Giotto) and 11 (Galileo), as well as by the EU-Central Asia Regional (EURECA) Programme. These studies revealed that cosmic dust consists of microparticles, nanoparticles and their aggregates. Their composition, size and physicochemical properties are origin-dependent. For example, dust particles in diffuse interstellar medium or dust clouds contain ice, carbon monoxide, nanoparticles of silicon carbide, amorphous calcium silicate and polynuclear aromatic hydrocarbons (PAHs) that exhibit properties like carbon dots as well as simpler organic structures. PAHs, which may have been formed only a short time after the Big Bang, are spread throughout the universe and may be associated with the formation of new stars and exoplanets [20].

1.2.4 Nanoparticles from Desert Surfaces

As written in *Smithsonian* magazine, the latest computer simulations of Earth's ancient climate show that the movement of tectonic plates that created the Mediterranean Sea and the Alps also sparked the drying of the Sahara Desert. The great and largest known desert on Earth was born nearly 7 million years ago as remnants of a vast sea called the Tethys Sea closed up. Deserts are a major permanent source of nanoparticles, which air currents lift into the atmosphere. Dust storms seem to be

the most important source of nanoparticles in the atmosphere. Dust storms carry nanoparticles present on the surface of the desert and migrate them to distant places, as aerosols are composed mostly (about 50%) of mineral dust [21].

Optical measurements of dust particles containing mostly soluble compounds of Fe, K and Co, taken in parallel with composition measurements, show that these particles are in the range of 400–600 nm. An analysis of particulate matter in the Gobi Desert in China and Korea by Chun *et al.*, [22] revealed that it has 24–32% Si nanoparticles, 5.9–7.4% Al nanoparticles, 6.2–12% Ca nanoparticles and <1% Fe nanoparticles.

1.3 Nano-Biosystem Consisting of Biotic Nanoparticles

Abiogenesis became impossible when photosynthetic cells added oxygen to the atmosphere. The oxygen in the atmosphere gave rise to the ozone layer which then shielded Earth from ultraviolet radiation. Newer versions of this hypothesis contend that the primitive atmosphere also contained carbon monoxide, carbon dioxide, nitrogen, hydrogen sulfide, and hydrogen. Present-day volcanoes also emit these substances.

Biological materials that evolved have supramolecular organization at the nano level, forming various shapes and sizes of complex combinations, giving them property to interact with light, water, temperature, pH and other molecules surrounding their matrix. At the bio-level, nanoparticles are synthesized biosystems and there are also biological organisms of nano size or having nano-organelles that synthesize custom-made nanoparticles for metabolism and survival [23]. Therefore, the existence of nanoparticles was obviously there when life evolved on this Earth. Individual particles of nano size, not connected to each other or something else, are also found in

many natural liquids (e.g., viruses, components of living cells, diatoms in sand grains present in the ocean).

The earliest organisms that evolved on this earth were thermophilic, i.e., able to dwell in hot environments. These organisms engaged in chemotropic metabolism and converted inorganic substances, such as sulfur and carbon, into energy to survive.

After the end of the Archean era, i.e., 2.5 billion years ago, the earth's atmospheric temperature reached 72 degrees Celsius. This is the maximum temperature at which photosynthesis can take place. According to Blank [24], about 2.7 to 2.9 billion years ago, stromatolites—photosynthetic bacteria that are the predecessor of today's bacteria—first appeared, which used photosynthesis to create energy without producing oxygen.

And the existence of nanoparticles in living systems evolved such as DNA, RNA, some proteins, cellular nano-organelles like ribosomes, mitochondria, nucleus, chloroplast, etc. Living beings that first evolved on Earth were very small; some of the known nano-size organisms that have existed since ancient times are discussed below.

1.3.1 Nanobe

Nanobes are filamental structures first found by Uwins *et al.*, [25] on Triassic (251 million and 199 million years ago) and Jurassic (199.6 to 145.5 million years ago) sandstones, and some rocks and sediments. They are the smallest form of life, with a diameter of 20 nm to 1 mm (Figure 1.2), showing a structure similar to actinomycetes. They may be a previously known form of *procell*, which does not have any DNA or RNA.

Nanobes are filamentous noncrystalline structures having an outer layer of cell wall. They are composed of C, O, and N and an electron dense region interpreted to be the cytoplasm and a less electron dense central region that is considered to represent a nuclear area because they show a positive reaction to three DNA stains; 49,6-diamidino-2 phenylindole (DAPI),

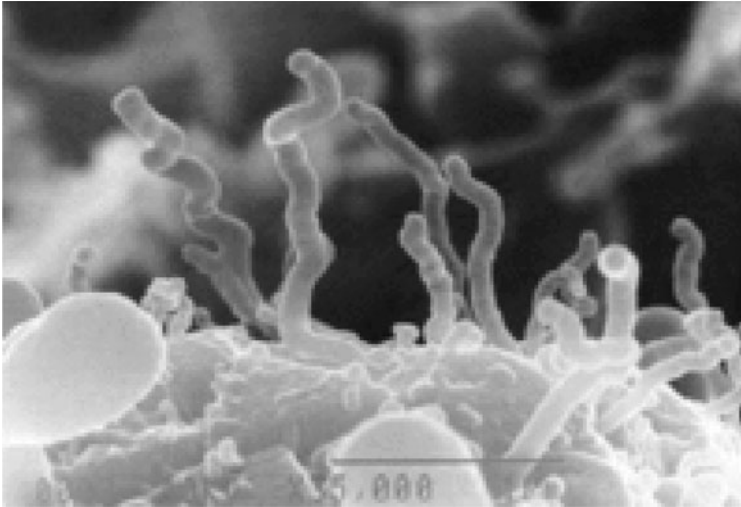


Figure 1.2 SEM image of a nanobe. Dr. Philippa Uwins found nanobe structures in Australian sandstones. (Photo courtesy of Philippa Uwins and the *Nanoworld Image Gallery*)

acridine orange, and Feulgen. They grow under aerobic conditions and at ambient temperatures.

1.3.2 Virus

Recording the origins of viruses has been difficult because there is no record of fossils of viruses. According to one hypothesis, viruses might have *evolved* from complex molecules of protein and nucleic acid before living cells first appeared on earth. The other hypothesis based on the analysis of the genes of many viruses suggests that they started as big bits of cellular DNA and then became independent. The third hypothesis is that these viruses came along very early on in evolution, and some of their DNA stuck around in the cells' genomes. The fact that some viruses that infect humans share structural features with viruses that infect bacteria could mean that all of these viruses have a common origin dating back several billion years. They are nano-size living beings (Figure 1.3).

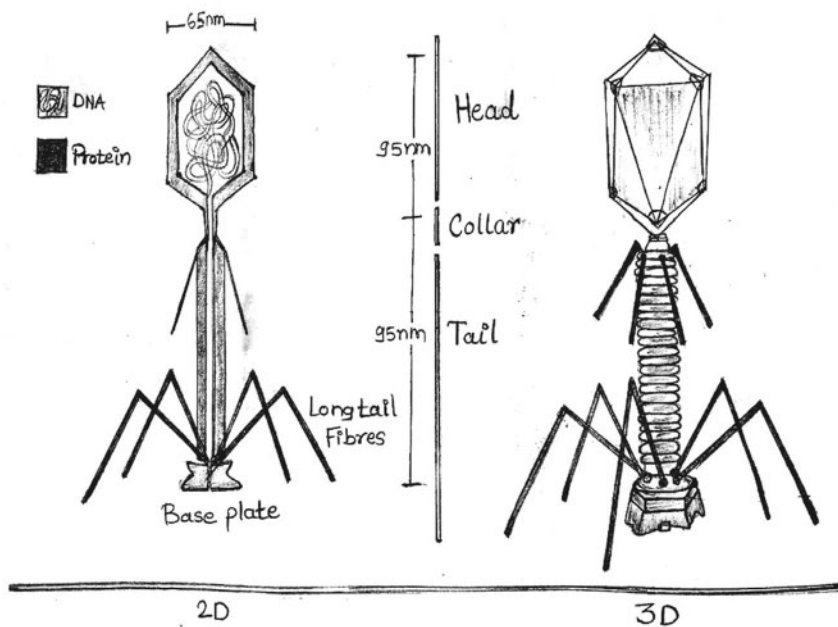


Figure 1.3 Schematic of a 2D (left) and 3D (right) T4 virus.

Parvoviruses are the smallest known viruses (18–28 nm). They are linear, non-segmented, single-stranded DNA viruses, having an average genome size of 5000 nucleotides, with a viral capsid made up of 2–4 proteins; whereas pandoraviruses (1000 nm) and pithoviruses (1500 nm) are the largest known viruses. Many consider viruses to be nonliving because they do not have a cellular structure, cannot metabolize by themselves, and require a host cell to replicate and synthesize new products. One can consider a virus as a nanoparticle existing at the junction of a living and nonliving entity. There is another such entity known as a prion (Figure 1.4), which is the smallest (≈ 10 nm) known infectious agent composed of proteins having 200–250 amino acids.

1.3.3 Bacteria

According to Blank [24], bacteria evolved 2.7 to 2.9 billion years ago. Microbes are known to generate nanoparticles in