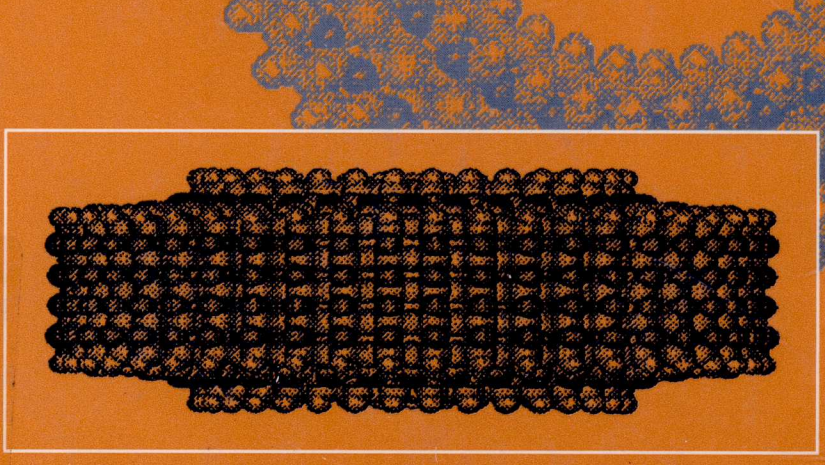
Edward A. Rietman

Molecular Engineering of Nanosystems



BIOLOGICAL PHYSICS SERIES

Edward A. Rietman

Molecular Engineering of Nanosystems

With 108 Illustrations

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BIOLOGICAL PHYSICS SERIES

Continued after index

"We are all lying in the gutter, but some of us are gazing at the stars."
—Oscar Wilde

This book is dedicated to the bodhisattvas helping us reach for the stars.

Series Preface

The field of biological physics is a broad, multidisciplinary, and dynamic one, touching on many areas of research in physics, biology, chemistry and medicine. New findings are published in a large number of publications within these disciplines, making it difficult for students and scientists working in the biological physics to keep up with advances occurring in disciplines other than their own. The Biological Physics Series is intended therefore to be a comprehensive one covering a broad range of topics important to the study of biological physics. Its goals is to provide scientists and engineers with text books, monographs and reference books to address the growing need for information.

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Oak Ridge, Tennessee

ELIAS GREENBAUM
Series Editor-in-Chief

Preface and Acknowledgments

Molecular nanotechnology allows us to build materials and systems with atomic and molecular precision. It posits molecular-scale machines that can manipulate individual atoms and molecules to build entirely new types of materials and molecular-scale machines. It points to biological life as existence proof that this level of technology is possible. For example, ribosomes are molecular-scale machines that read RNA as if it were a molecular-scale tape. From this coded information, it manufactures proteins and then assists in folding of the protein to make sure the newly assembled molecular part conforms to the correct three-dimensional configuration.

There are several scientific fields converging on developing nanotechnology. Some key fields of science that are having an impact on nanotechnology are physics, chemistry, and biology. This book will mostly discuss the chemical physics associated with designing and understanding molecular systems. Other areas discussed, briefly, are proximity probe methods and genetic engineering. These, along with chemical methods, will converge for the first generation of molecular nanotechnology. I hope the book will be useful to computer and system scientists as a tool in modeling molecular systems.

Several people have helped in the preparation of this book. First, and foremost, I thank my wife, Suzanne Harvey. This was not an easy book to produce, and she exhibited great patience with me when I needed to work on the manuscript. Then, at other times, when she wanted me out of the way, she reminded me that I had a book to write. Together, we got it done. While doing all this, she taught me kindness.

Libraries are the most important repository of information for a civilization, and library scientists have one of the most important jobs in any civilization—helping us navigate through the labyrinths of the knowledge base. I thank Liz Zimmerman, a library scientist at Bell Labs, for many sources and conversations. Without her help, this book would not have been possible.

After the manuscript was finished, Dr. J. Stross Hall, of the Institute for Molecular Manufacturing, read many of the chapters and made helpful comments on ways to improve the manuscript.

Professor Mark Andrews of McGill University exceeded everyone's expectations on editing the manuscript. His comments strongly influenced the final draft. Any errors or remaining unclear passages are my responsibility.

I also thank Maria Taylor, my editor at Springer, for her unending patience. I am sure she must have thought at times that this book would never be finished. And I thank the copy editor(s) for the hard work they put into this manuscript.

Edward A. Rietman
Brussels, Belgium
January, 2001

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1
Enabling Technologies for Molecular Nanosystems

Feynman (1960) first proposed a molecular-scale technology. Drexler (1981, 1986, 1992) went far beyond that proposal and described some of the limitations of these molecular machines. Specifically, he proposed a machine known as an *assembler*. An assembler in this context is a machine that has the ability to construct essentially anything we program it to construct. Macroscale versions of these machines are called Santa Claus machines (Calder, 1978) and von Neumann machines (Freitas and Gilbreath, 1982). In this chapter, we will examine the rationale for that conjecture and some exploratory engineering leading toward that long-range goal. Subsequent chapters will review progress to date with a focus on the chemical enabling technologies that will bring this long-range goal to fruition.

1.1 Engines of Creation

Chemistry is the mother of all technologies. For example, only through our understanding and advances in chemical and molecular sciences have we been able to make technological breakthroughs in computer engineering and biotechnology. The quantum physics knowledge behind the computer revolution would be theoretical without the chemical knowledge of modifying surfaces of single crystals. The key component in modern computers, and most electronic systems, is the microchip. These chips are built by chemical modification of the surface of single crystals of silicon. The foundations of modern genetic engineering, pharmacology, medicine, and biotechnology are all based on chemical knowledge. If we can assemble our technologies at the atomic and molecular levels, we will achieve a precision in construction heretofore not even dreamed of. We will literally be able to dictate where each atom and each molecule will be placed. Whole realms of possibilities are opened if we can have a technology, or better yet, a tool, that enables us to assemble matter in this fashion. Drexler recognized this, and it is reflected in the subtitle of his 1986 book—*Engines of Creation: Challenges and Choices of the Last Technological Revolution.*

This is the basic idea that Drexler proposed in his 1986 book. In his 1981 paper, he drew a number of parallels between this idea and biological systems. For example, ribosomes are complex molecular machines built from proteins. These machines, when placed in an appropriate medium with molecular feedstock and other raw materials, can read a molecule of DNA—like reading a data tape—and assemble proteins. These new proteins can be used for structural purposes, act as chemical process assistants, and even become components for more ribosomes. Ribosomes are almost the universal assembler we seek. A universal assembler would allow us to build anything with atomic precision. Drexler's hypothesis is supported not by theoretical arguments alone but by existence proof in the form of biological life. The assemblers in the biological world (ribosomes) are able to assemble a huge variety of biological organisms from single cells to redwood trees to human brains. What if we could capture that ability and program the machines to assemble anything?

How can we get from where we are now, with our impressive but limited chemical knowledge, to the point where we can achieve this long-range goal? We need a classification system for different types of nanotechnology. Diamond is an excellent structural material, and it would be ideal as a building material for many systems. A diamondoid-based nanotechnology (Drexler, 1992) we will call the diamond age. It would be a second-generation nanotechnology. Figure 1.1 shows a bearing built from carbon atoms. This is an example of the molecular-scale components that will be assembled during the second generation. The first-generation of nanotechnology will be the bootstrap to get us to that "last technological revolution." We need a hybrid nanotechnology to get us from where we are now to there. This first-generation nanotechnology will likely be based on our combined knowledge of chemical, biological, and physical sciences. Appropriate topics

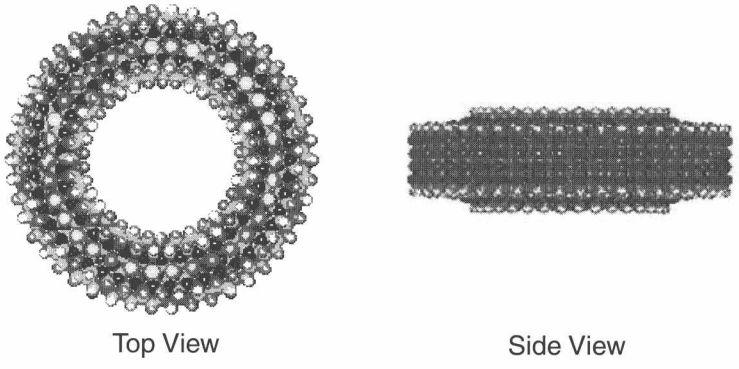

FIGURE 1.1. Example of a bearing that will be available during the second generation of molecular nanotechnology.

for study then are solution phase chemistry, protein engineering, and scanning probe technologies.

1.2 Selected Reviews of Nanotechnology

If in fact our long-range goal is to build an assembler, then we need to do more than speculate on its capabilities but also describe some of the components needed to make molecular-scale machines. In this section, I will review some of the papers from the journal *Nanotechnology* and from a few published conference proceedings. The basic ideas involved in mechanosynthesis or mechanochemistry are to place atoms at selected sites in larger molecular, structures (Drexler, 1992). The main purpose of this section is to bring to the reader's attention various possibilities and to start the reader thinking about molecular-scale machinery.

Figure 1.1 shows an example of molecular-scale bearings that have been described by Drexler (1992) and Merkle (1993). With molecular bearings, a lubricant molecule is essentially a foreign particle and is equal to grit in a macroscale bearing, but using atomically precise bearings the issue of lubrication is nonexistent. In order to ensure that there is no energy barrier to rotation, the shaft should have m-fold symmetry and the sleeve should have n-fold symmetry, and m and n should have a small GCD (greatest common divisor). The bearing shown in the figure has $m = 13$ and $n = 20$. The barrier height to rotation is less than 0.004 kcal/ mole, and the thermal noise is about 0.6 kcal/mole. The rotation period is 1/230.

Building molecular machines based on diamond will necessarily involve manipulating hydrocarbons, and therefore hydrogen abstraction. Drexler (1992) suggested a hydrogen abstraction tool for the end effector on an assembler. Basically, he proposed an acetylene radical as the main reactive tool. The acetylene tool (Figure 1.2) is ideally suited for the task. It must have a high affinity for hydrogen. It must not have surrounding groups that

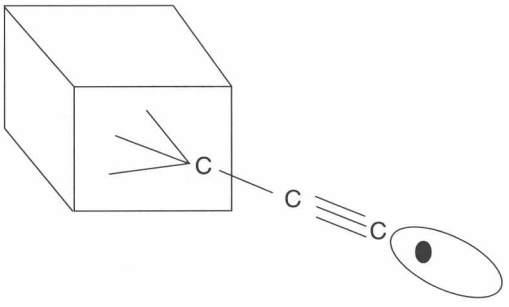

FIGURE 1.2. Hydrogen abstraction tool attached to a molecular substrate (after Musgrave et al. 1991).

TABLE 1.1. Bond dissociation energies (after Musgrave et al. 1991).

R—H	Energy
H—H	102
CH_3—H	105
$(CH_3)_3C$—H	93
C_6H_5—H	111
HCC—H	126

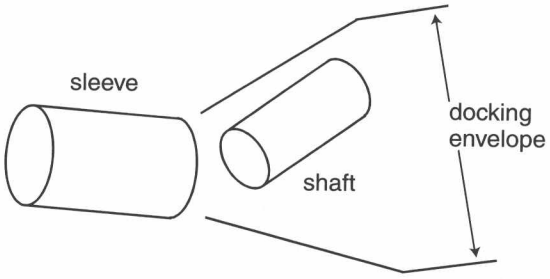

FIGURE 1.3. The docking envelope for a molecular shaft and sleeve.

could result in steric hindrance with the work site, and it must be mechanically and chemically stable. The bond dissociation energies for hydrogen in several molecular arrangements are given in Table 1.1. The net result from the hydrogen abstraction by the tool is that the triple bond is turned into a double bond. The tool now must either be discarded (a series of tools could be brought into the work environment) or regenerated. The following equation shows the net effect on the hydrogen abstraction tool.

$$—C{\equiv}C^* + H—CR_3 \rightarrow —C{=}C—H + {}^*CR_3$$

Merkle (1997) has proposed a complete set of reactions for hydrogen removal and addition. He has also discussed a complete set of metabolism reactions by a hydrocarbon assembler.

An interesting question concerning the assembly of molecular bearings is the docking of the sleeve and the shaft. Tuzun et al. (1998) raised the question of determining the positional and orientational approach tolerances of a shaft and sleeve (Figure 1.3). This is important for understanding the degree of external control associated with the assembly. Not surprisingly, they found that the size of the docking envelope varied directly with the sleeve, and changing the potential energy surface had only minor effects.

Once the shaft is in the molecular bearing, one would like to understand the rotational dynamics. This can be done by studying the potential gradient of the interaction energy. Tuzun et al. (1995) and Sohlberg et al. (1997) have done this using classical and molecular-dynamics simulations

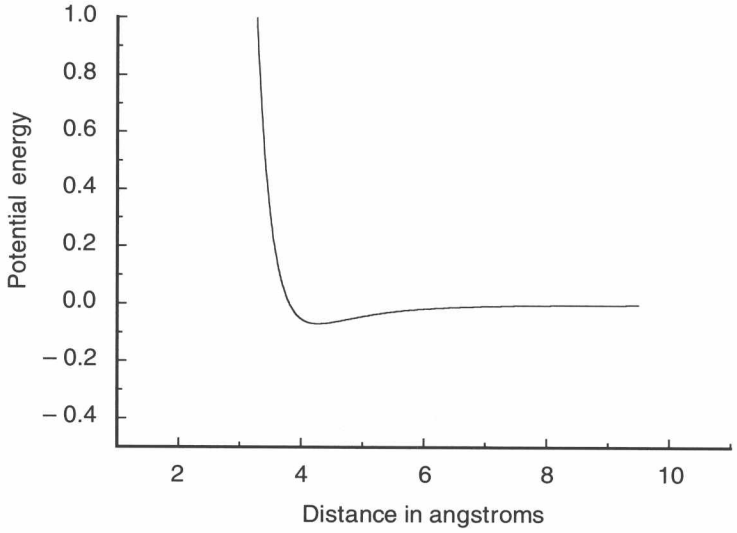

FIGURE 1.4. Lennard-Jones 12-6 potential.

(see also Han et al. 1997). The common starting point for studies of this type is the Mie potential or the Lennard-Jones 12-6 potential shown in Figure 1.4.

$$\varphi(r) = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right). \tag{1.1}$$

The potential energy $\varphi(r)$ is a function of the radius. When $\sigma = r$, the potential is zero. (More chemical physics detail is given in later chapters.)

The conclusion of these studies is that classical rigid-body dynamics and semiclassical mechanics are quite sufficient for studying the rotational dynamics of molecular components. Most of the total energy available to the bearing is in the spin of the shaft, and the rotation is superrotary, as suggested by Feynman (1960).

Now that we have shafts rotating in bearings, what can we do with them? DeMara et al. (1994) demonstrate a helical latch for Boolean logic operations. They develop a rotating shaft with small knobs and dents at various levels. These knobs and dents encode the 1s and 0s for logic operations.

So how can we build these systems? This book is about chemical methods for enabling molecular nanosystems. In addition, there are two other key technologies, protein engineering and scanning probe methods. Protein engineering is discussed in Chapter 6. Scanning probe methods will be discussed briefly in the next section.