SELF ASSEMBLY

The Science of Things That Put Themselves Together

John A. Pelesko

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Preface

Nanotechnology has been hailed as the “21st Century’s great leap forward in scientific knowledge.” It’s claimed that nanotechnology “is destined to become the core technology underlying all of 21st century medicine” and that it will “cure cancer and replace fossil fuels” and yet that these advances will only “seem a minor part of the whole.”[1] I don’t know where nanotechnology will take us and I don’t know whether the claims of its most avid proponents will prove true, but I do know that the science of *self-assembly* offers the most promising route to true molecular nanotechnology available today. This book is about self-assembly.

As an enabling technique for nanotechnology, self-assembly replaces *top down* fabrication with the possibility of *bottom up* fabrication. It’s the difference between building nanoscale structures molecule by molecule using the equivalent of nano-chopsticks, and letting molecules do what they do best, self-assemble themselves into useful structures. But, to fully utilize this new technique, we must understand what it is that nature does when she builds objects by self-assembly. In recent years, a host of scientists and engineers, from every imaginable discipline, have been working to figure this out. And, more importantly, they’ve been working to put nature’s principles to use in the laboratory and eventually in the factory. While much remains to be done, much has been accomplished. It’s these accomplishments that we’ll look at in this book.

This book is divided into three parts. This structure reflects the natural progress of the science of self-assembly. We begin in *Part I: The Natural World*, by examining just what it is that nature does and what we can say about how she does it. With this inspiration, we move on to *Part II: Engineered Systems*, and examine the many different ways in which scientists are learning to exploit nature’s techniques. Finally, in *Part III: The Future*, we examine the developing theoretical underpinnings of self-assembly and the latest varied advances in the field. It is through this pairing, theory and experiment, that the science of self-assembly is moving forward.

But, self-assembly is not just an enabling technique for nanotechnology. The science of self-assembly is also a way of understanding the natural world, understanding biology, understanding physical phenomena, and perhaps, ul-

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[1] These quotes are from *Nanotechnology* by Wilson et al. the article *Nanomedicine* by Ralph Freitas, and the article *Why should you care about molecular nanotechnology?* by K. Eric Drexler, respectively.

timately, understanding the origin of life itself. Consequently, this book often goes beyond nanotechnology - we examine systems at all length scales. The greatest practical application of these efforts may lie in nanoscience, but the most important implications of the ideas explored here may lay elsewhere.

Self Assembly: The Science of Things that Put Themselves Together, is an introduction to this exciting field. It is intended for use by working scientists and engineers in every discipline, as well as students studying science, engineering, or mathematics who wish to understand the science of self-assembly as both the great enabling technology for nanotechnology and as a viewpoint for understanding many features of the natural world.

Prerequisites

As with nanotechnology in general, self-assembly does not fit into any convenient academic box. Research in self-assembly is being conducted by individuals in every imaginable discipline. To grasp the details of every study that has been done one would need an extensive background in chemistry, physics, biology, computer science, mathematics, and engineering. Of course, for most of us, that's just not possible. So, as much as possible, this book has been written to be self-contained. Concepts from different disciplines are introduced as needed and explained in sufficient detail to allow the reader to grasp the main ideas of the text. The Related Reading section at the end of each chapter gives suggestions for following up on topics or filling in needed background. References to all of the original journal articles discussed in the text are given at the appropriate point. The reader may find the glossary at the end of the text useful; there is also an appendix that can be used to quickly introduce the reader to the calculus of variations.

Chapter Interdependence

This book is meant to be read sequentially. Ideas build from chapter to chapter, examples become increasingly complex, and exercises rely on information presented in earlier chapters. Nonetheless, instructors may find that the background of their students allows them to skip certain chapters or integrate the material of later chapters with the material of former chapters. For a class of students with little mathematical background, Chapter 9 may be skipped entirely. The basic modelling ideas introduced in Chapter 9 are introduced elsewhere, but with much less detail. For an advanced class, the instructor may wish to include material from Chapter 9 earlier in the discussion. For example, the graph grammar model of Chapter 9 can be discussed immediately following Chapter 7. Similarly, the conformational switch model of Chapter 9 can be brought in as early as Chapter 3.

Profiles

In every chapter of this text you'll find a one-page profile of a notable individual who has made important contributions to the field of self-assembly. Unfortunately, there are only ten chapters and hence I could only include ten individuals. There are many more noteworthy people working in this area than these ten. Some may find my choices here unusual. With the exception of Richard P. Feynman, profiled in Chapter 1, all of the profiles are of active researchers. Many of them are young, several (gasp!) are not even yet full professors. Or, professors of any kind. Yet, each individual profiled has something important to say about the science of self-assembly. I hope you'll enjoy meeting them.

Try it Yourself

Self-assembly lends itself to hands-on activities that can greatly enhance your understanding and feel for the problems and challenges of this field. Scattered throughout the text you'll find *Try it Yourself* exercises. Each of these requires a minimum of experimental expertise, can usually be built with everyday or easily acquirable materials, and serves to demonstrate at least one key principle discussed in the text. With the aid of many undergraduate students working in our lab at the University of Delaware, I've carried out all of the experiments described here. If you have difficulty following the instructions or getting your system to work as described please feel free to contact me through the web page for this text. The web page also contains video of several of the experiments and links to other pages illustrating these experiments.

Related Reading

At the end of each chapter you'll find a section entitled *Related Reading*. These sections contain pointers to books, journal articles, and web pages that relate to and expand upon the material in the given chapter. I've resisted the temptation, succumbed to by far too many authors, to simply include lists of "classic" works in a given area. Rather, I've followed a strict policy of only recommending books, articles, and web pages that I've read myself, found accessible, and found useful.

The World Wide Web

In only a fraction of my lifetime the world wide web has evolved from a novelty to an essential feature of any text such as this. To accompany this book, I've developed a web page, www.pelesko.com, that contains links to the numerous web sites mentioned in the text as well as other resources and information about self-assembly. As you read the text, you'll encounter several systems that can only truly be appreciated by watching them in action. Links to video of these systems may be found on the web page for this book. When you reach these points in the text, I encourage you to go to the web page and view the video of the relevant system.

A Note on Terminology

A majority of authors seem to use a hyphen when referring to "self-assembly" or "self-assembled" systems. A minority omit the hyphen. With the exception of the title, I've deferred to the majority.

Acknowledgments

I am indebted to many people whose advice, support, and help during the writing of this book have been invaluable. Thanks to my editor at CRC Press, Sunil Nair, and all of the staff at CRC, especially Helena Redshaw. Thanks to Rob Ghrist for many conversations that forced me to think broadly about the meaning of self-assembly. Thanks to the many students who have been indirectly or directly involved in my exploration of self-assembly. Especially, the students of Math 824 in Spring 2004, and the many undergraduate and graduate students who have worked in the MEC Lab. Among these, Katy Sharpe, Janine Janoski, Lauren Rossi, Dan Cargill, Tom Fleetman, Derick Moulton, and Regan Beckham deserve special mention.

I owe a special debt of thanks to all of those who agreed to be profiled in this book. Especially, Erik Klavins, Eric Winfree, Paul Rothemund, Saul Griffith, Ned Seeman, and John Reif for their gift of time.

Their are many wonderful people I have interacted with over the years who have shaped my career. I would especially like to acknowledge Greg Kriegsmann and Daljit Ahluwalia for the environment they created at the New Jersey Institute of Technology. Thanks to my colleagues at the University of Delaware, especially Toby Driscoll and Lou Rossi for making UD such a fun place to work. I need to thank my high school English teacher, Julius Gottilla, who agreed to finally read something I wrote as long as his name appeared in the acknowledgements. We'll see. I'd like to thank Julia Lee Pelesko for "lending me a hand" with Chapter 3. I'd like to thank John R. Pelesko for letting me use his bath time to explore bubble rafts and inspiring the start to Chapter 2. But mostly, I'd like to thank Julia and John-John for the time I spent writing that I could have otherwise spent with them.

This book is dedicated to the memory of John Pelesko, Sr., 1916-2005, hobo, soldier, cowboy, trucker, fisherman, father, grandfather, and master storyteller.

John A. Pelesko
Newark, Delaware
January 2007

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Chapter 1

Introduction

> *Though men now possess the power to dominate and exploit every corner of the natural world, nothing in that fact implies that they have the right or the need to do so.*
>
> Edward Abbey

1.1 Self-Assembly

This is a book about an idea. An observation, really. Simply stated - *No one put you together.* Or the trees outside my window, or the groundhog under my shed, or the simplest bacteria, or the largest whale, or the salt on my popcorn, or the soap bubbles I blow for my children. Somehow, remarkably, all of these things, some alive, some not, *put themselves together.* We call this process, this idea, *self-assembly.* Today, this simple observation has become the basis for one of the most exciting research directions in science, and more modestly, the subject of this book - *Self Assembly: The Science of Things that Put Themselves Together.*

Understanding self-assembly requires the efforts of researchers from almost every imaginable discipline. Biologists are busy unravelling nature's secrets, yielding a deeper understanding of how she effortlessly produces intricate structures from simple building blocks. Chemists are coaxing molecules to form into ever larger and more complex systems. Engineers are developing new manufacturing methods, pushing the boundaries of engineered systems to the nanoscale. Computer scientists are learning to compute with DNA, while mathematicians are developing models to help solve the difficult design problems we encounter as we learn to harness the power of self-assembly. The study of self-assembly is truly a multi-disciplinary endeavor. If you want to understand what self-assembly is, if you are excited by the simple idea that no one put you together, and if you are prepared to examine this subject from a wide variety of perspectives, then this book is for you.

But, self-assembly is a slippery concept. Patterns and structures abound in nature. What is self-assembled? And, just as importantly, what is not? Consider the picture of the barred spiral galaxy NGC 1365 shown in Figure

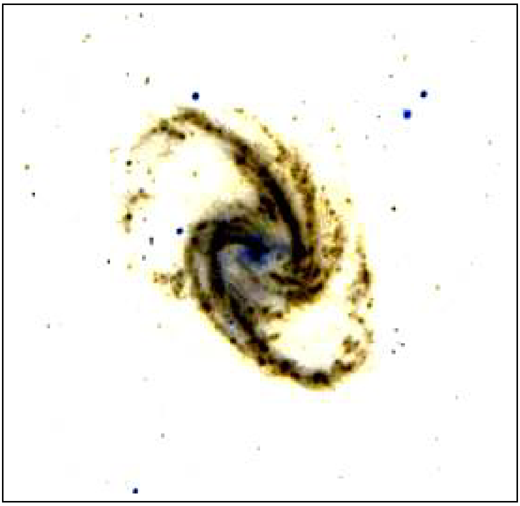

FIGURE 1.1: Barred Spiral Galaxy NGC 1365. Colors have been reversed to highlight the spiral structure. Credit: NASA Jet Propulsion Laboratory.

1.1. The spiral structure is evident, and we know that this structure is made up of billions of individual particles, stars. Under the influence of gravitational forces, these billions of stars have organized themselves into the structure we see in Figure 1.1. Is this self-assembly? Or, consider the Von Karman vortices over Alaska shown in Color Plate 11.2. Again, a pattern is evident. We know that these structures were formed as the atmosphere interacted with Alaska's Aleutian Islands. Is this self-assembly? On a smaller scale, consider the fluoride crystal of Color Plate 11.6, or the bismuth crystal of Color Plate 11.4. Should crystal growth be considered self-assembly? Or, we can look to living systems. Did the pattern of spots on the Asian multicolored lady beetle, Color Plate 11.5, arise by some form of self-assembly? Was the structure of the single celled eukaryote Oxytricha Trifallax, Figure 1.2, built by some self-assembly process?

Clearly, in nature, the potential range of phenomena that could be called "self-assembly" is enormous. How about in man-made systems? Unfortunately, researchers in almost every discipline use the term "self-assembly," and even more unfortunately, they often use it to describe very different ideas. We need to focus. We need a guiding principle, a concrete definition, and a goal.

In this book, our guiding principle is this - we believe there is a growing body of researchers, from a wide variety of disciplines, investigating something new and exciting called "self-assembly," and ultimately, although their approaches may differ, they are talking about the same thing. It's a bit like the fable of the six blind men and the elephant[1]. Chemists are feeling the tail and declaring "supermolecular chemistry!" Biologists are squeezing the nose and

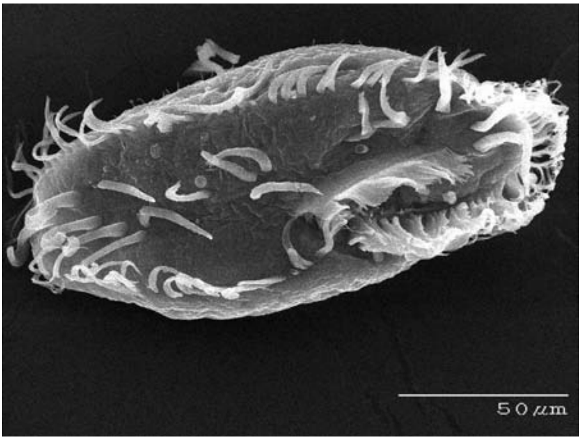

FIGURE 1.2: The single celled eukaryote Oxytricha Trifallax. Credit: National Institutes of Health.

exclaiming "protein folding!" Meanwhile mathematicians are flapping the ears and muttering about Wang Tiles and Universal Turing Machines. But, in the end, it's all elephant. In this book, the belief that a new cross-cutting discipline is emerging and that this discipline should be called "self-assembly" will serve as our guide.

Our goal is more concrete; we want to understand how nature self-assembles structures, we want to understand her principles and techniques, and, we want to learn how to use self-assembly to build engineered systems. The structure of *Self Assembly: The Science of Things that Put Themselves Together* reflects this goal. In *Part I: The Natural World*, we'll take a closer look at natural self-assembling systems. We address the question - What does nature do and how does she do it? We'll begin, in Chapter 2, with inorganic systems and examine in detail topics such as crystal growth, soap films, and micelles. In Chapter 3, we'll look at organic systems and see how nature builds viruses, proteins, and ribosomes. We'll introduce the protein folding problem and see how nature uses energy minimization to produce a remarkable range of biologically functional molecules. In the concluding chapter of Part I, Chapter 4, we'll examine what we've learned and abstract the principles nature uses to self-assemble structures.

In *Part II: Engineered Systems*, we ask the question - What can we build now and how do we do it? We'll see how nature's principles are being applied by physicists, chemists, biologists, and engineers as they induce cubes to self-assemble from DNA or electronic circuits to self-assemble from millimeter-scale polyhedra. In the first chapter of Part II, Chapter 5, we examine the simplest engineered self-assembling systems. What we learn from these simple systems allows us to understand the more complicated systems of Chapters 6, 7, and 8. In Chapter 6, we'll see how capillary forces, magnetic forces, and the principle of energy minimization are used to design functional self-assembling systems. In Chapter 7, we focus on dynamic systems, i.e., those that self-assemble and maintain organization only while dissipating energy. Finally, in Chapter 8, we address the myriad ways in which DNA is being exploited in the design of self-assembled systems.

In the final part of this book, *Part III: The Future*, we ask the question - How do we realize the full promise of self-assembly? We'll revisit the challenges in understanding how nature self-assembles systems and the challenges in designing engineered self-assembling systems that we encountered in the first two parts of this book as we survey the various theoretical approaches and the latest experimental approaches to overcoming these challenges. Hopefully, by this point, you'll have a clear understanding of what self-assembly is, and be fully prepared to delve into the primary literature in the field.

Now, we have our principle and we have our goal, but we still need our definition. Just as Aristotle grappled with parsing the difference between the animate and the inanimate, or between man and animal, scientists today have grappled with how best to define the burgeoning field of self-assembly. While no present definition of self-assembly approaches the elegance of Aristotle's definition of man as a "rational animal," they are all worth a look.

In a relatively early paper on self-assembly Hosokawa et al. [62] refer to nature in an attempt to define self-assembly:

> Viruses and bacterial flagella are constructed automatically out of protein subunits. This phenomenon is called self-assembly, which is a powerful technique applicable to microfabrication.

They go on and enumerate the conditions necessary for a system to self-assemble:

> To achieve self-assembly, the following conditions must be met: generating bonding forces, bonding selectively, and moving the parts randomly so that they come together by chance.

A later simpler definition is offered by Campbell et al. [25]:

> Spontaneous assembly, often called "self-assembly," refers to aggregation of particles into an organized structure without external assistance.

Equally simple definitions have been offered by several others. Aggarwal et al. states [3]:

> Self-assembly is the ubiquitous process by which objects autonomously assemble into complexes.

John H. Reif [102] also offers a straightforward definition:

> Self-assembly is a process in which small objects autonomously associate with each other to form larger complexes.

The group led by George M. Whitesides of Harvard University has offered several definitions. In a 2002 review paper [139] they ask the question "Is anything not self-assembly?" and offer this definition in an attempt to distinguish between self-assembly and formation:

> ...we limit the term to processes that involve pre-existing components, are reversible, and can be controlled by the proper design of the components.

Finally, in a 2006 publication [41] the group led by Bartosz A. Grzybowski at Northwestern University defined self-assembly as:

> ...we limit SA to the spontaneous formation of organized structures from many discrete components that interact with one another directly and/or indirectly through their environment. In addition, the assembling components may also be subject to various global (confining) potentials such as externally imposed electromagnetic fields or chemical gradients.

Freely borrowing from all of the above, in this book we define self-assembly as follows. **Self-assembly** *refers to the spontaneous formation of organized structures through a stochastic process that involves pre-existing components, is reversible, and can be controlled by proper design of the components, the environment, and the driving force.* As we make our way through this text, we'll see the necessity of each of the elements of this definition. The word "organized" will allow us to distinguish between self-assembly and aggregation processes. The emphasis on "pre-existing components" will allow us to distinguish between self-assembly and pattern formation while the words "stochastic," "design," "environment," and "driving force" push us towards an understanding of those features of self-assembly necessary to reach our goal of designing engineered self-assembling systems.

Finally, within the class of phenomena that we call self-assembly, it is useful to emphasize three particular subclasses. *By* **static self-assembly** *we mean that subclass of self-assembly processes that leads to structures in either local or global equilibrium. By* **dynamic self-assembly** *we mean that subclass of self-assembly processes that leads to stable non-equilibrium structures.* That is, these structures exist only so long as the system is dissipating energy. *By* **programmed or programmable self-assembly** *we mean that subclass of self-assembly processes where the particles of the system carry information about the final desired structure or its function.*

Profile - Richard P. Feynman

With the title of his 1992 biography of Richard P. Feynman, author James Gleick, succinctly described this Noble-Prize winning physicist and father of nanotechnology: *Genius*. Feynman was born in New York City on May 11th, 1918. He grew up in Far Rockaway, where even as a youngster he established a reputation for his unbridled curiosity, his sense or humor, and a talent for mathematics. As an undergraduate, Feynman attended the Massachusetts Institute of Technology. He received his Ph.D. from Princeton University in 1942. He subsequently held appointments at Cornell University and the California Institute of Technology. During World War II, Feynman played a key role in the Manhattan Project, helping to develop the first atomic bomb. In 1965, Feynman won the Noble Prize in Physics for his work on quantum electrodynamics. A far-ranging thinker, Feynman is remembered for much more than just his contributions to quantum theory. He made fundamental discoveries in superfluidity, the theory of quarks, and the theory of the weak nuclear force. He served on the President's commission investigating the space-shuttle *Challenger* disaster. His elegant demonstration of the reason for the shuttle failure, dipping an O-ring in a glass of ice-water, illustrated his ability as an educator and his talent for making difficult concepts clear. The Foresight Nanotech Institute created two prizes named after Richard P. Feynman, acknowledging his role in launching the field of nanotechnology. The Foresight Institute Feynman prize is awarded annually to one theoretician and one experimentalist who has advanced the achievement of Feynman's vision for nanotechnology. The as of yet unclaimed Feynman Grand Prize will be awarded to the first team who designs and builds a nanoscale robotic arm and a nanoscale computer.

No brief biography or profile can truly capture the essence of Richard P. Feynman or the reason for the extent of his influence on both the scientific and lay communities. Feynman's advice to the Caltech graduating class of 1974 may do a better job:

> *The first principle is that you must not fool yourself – and you are the easiest person to fool.*

Further Reading There have been numerous books written about Richard P. Feynman. The best biography is the one by Gleick [48]. However, we are also fortunate to have access to Feynman through his own writing and recorded lectures. He recounts many of his adventures as a youth, at MIT, and as a Ph.D. student in his bestselling 1985 autobiography, *Surely You're Joking, Mr. Feynman!* This was followed by the entertaining *What Do You Care What Other People Think?* in 1988. Many of his lectures were captured on audio tape and have been released on compact disc. Several are available as free streaming-video on the internet. Links may be found on the web page for this book. Finally, any serious student of physics must own the three volume set, *The Feynman Lectures on Physics* [42].

1.2 Why Now?

Now that we have a working definition of self-assembly, the question still remains: Why the sudden explosion of interest in this field? That self-assembly has thoroughly captured the interest of the scientific community was made clear with the publication of the 125th anniversary issue of *Science*. To celebrate this anniversary, the editors identified twenty-five big questions and one-hundred little questions likely to shape the course of scientific research for the next one-hundred and twenty-five years. Listed among the big questions, right alongside "What is the universe made of?" "Can the laws of physics be unified?" and "Are we alone in the universe?" we find "How far can we push chemical self-assembly?" How did self-assembly, a field yet barely defined, rise to prominence so quickly? This sudden ascent may be ascribed to a confluence of developments in science and engineering.

First among these is the advent of *nanotechnology*. Nanotechnology deals with the very small, with the construction of structures characterized by length scales of less than 100nm. To get a sense of this scale, let's contrast a nanoscale machine that we'll study in Chapter 3, the ribosome, with some everyday small objects. A typical ribosome measures about 25nm in diameter. Keep in mind that the ribosome is a *fully-functional machine*. Contrast the size of the ribosome with that of a typical grain of sand. On average, sand is about 500μm in diameter. That's $500,000$nm, $20,000$ times the size of the ribosome. Human hair brings us a little closer. With an average diameter of around 50μm or $50,000$nm, that's only 2000 times the size of the ribosome. Nanotechnologists are attempting to replicate nature's ability to make useful machines, such as the ribosome, on the nanometer scale.

The possibility that humans could build nanoscale machines was first recognized by Richard P. Feynman and discussed in a famous lecture at the 1959 annual meeting of the American Physical Society. In a passage on biology, Feynman captured much of what excites self-assembly researchers today:

> The biological example of writing information on a small scale has inspired me to think of something that should be possible. Biology is not simply writing information; it is *doing something* about it. A biological system can be exceedingly small. Many of the cells are very tiny, but they are very active; they manufacture various substances; they walk around; they wiggle; and they do all kinds of marvellous things – all on a very small scale. Also, they store information. Consider the possibility that we too can make a thing very small which does what we want – that we can manufacture an object that maneuvers at that level!

While he did not anticipate or discuss the notion of self-assembly, Feynman did recognize that the problem of actually making nanoscale systems was a

TABLE 1.1: Landmarks in the History of Nanotechnology Reproduced with permission from *Modeling MEMS and NEMS*, Pelesko and Bernstein [99].

1940s	Radar drives the development of pure semiconductors.
1959	Richard P. Feynman's famous "There's plenty of room at the bottom" lecture.
1960	Planar batch-fabrication process invented.
1964	H.C. Nathanson and team at Westinghouse produce the resonant gate transistor, the first batch-fabricated MEMS device.
1970	The microprocessor is invented, driving the demand for integrated circuits ever higher.
1979	The first micromachined accelerometer is developed at Stanford University.
1981	K. Eric Drexler's article, *Molecular Engineering: An Approach to the Development of General Capabilities for Molecular Manipulation*, is published in the Proceedings of the National Academy of Sciences. This is arguably the first journal article on molecular nanotechnology to appear.
1982	The scanning tunneling microscope is invented.
1984	The polysilicon surface micromachining process is developed at the University of California, Berkeley. MEMS and integrated circuits can be fabricated together for the first time.
1985	The "Buckyball" is discovered.
1986	The atomic force microscope is invented.
1991	The carbon nanotube is discovered.
1996	Richard Smalley develops a technique for producing carbon nanotubes of uniform diameter.
2000s	The number of MEMS devices and applications continually increases. National attention is focused on funding nanotechnology research and education.

difficult one. In some sense, in the fifty years since Feynman's lecture, we've made rapid progress in tackling this problem. Today, we have batch-fabricated microprocessors containing nanoscale transistors in our cell phones. We have new tools such as the scanning tunnelling microscope (STM) and the atomic force microscope (AFM) that allow us to examine and manipulate matter on the nanoscale. And, we have new nanostructured materials such as the carbon nanotube that promise to revolutionize materials science. But, researchers in nanotechnology have come to realize that for all of the progress we've made, we still rely on "top-down" construction methods. When Eigler and Schweizer [37] famously wrote the letters "IBM" on a layer of nickel using individual xenon atoms, a true tour-de-force in nanoscale engineering, they still used a fundamentally primitive and decidedly unbiological technology. In essence, Eigler and Schweizer used their STM as a pair of very small tweezers and wrote "IBM" much as I might spell out my name on my desk with grains of salt. Researchers in nanotechnology have come to realize that if we are to truly realize Feynman's vision, we not only have to learn to build small, we have to learn to build small in the way that nature builds small. We need to coax our systems to self-assemble.

In parallel with progress in nanotechnology fuelling the need for understanding self-assembly, key developments in mathematics, computer science,

TABLE 1.2: Landmarks in Self-Assembly

1930s	Alan Turing develops the theory of universal computation.
1950s	John von Neumann develops theory of automata replication.
1953	James D. Watson and Francis Crick discover the structure of DNA.
1955	H. Fraenkel-Conrat and R.C. Williams self-assemble the tobacco mosaic virus in a test tube.
1957	Penrose and Penrose construct a simple self-replicating system.
1961	Hao Wang develops "Wang Tiles" demonstrating the equivalence of tiling problems and computation.
1991	Nadrian C. Seeman and Junghuei Chen self-assemble a cube from DNA.
1994	Leonard Adleman launches the field of DNA computation by using DNA to solve a Hamiltonian path problem.
1996	Kazuo Hosokawa's group demonstrates microscale self-assembly using surface tension.
2000	George M. Whitesides's group self-assembles electrical networks from millimeter scale polyhedra.
2004	William Shih adapts the methods of Seeman to self-assemble a DNA octahedron.
2004	Eric Winfree and Paul Rothemund self-assemble a Sierpinski triangle from DNA demonstrating that self-assembly may be used for computation.
2000s	Self-assembly research explodes drawing the interest of researchers from every imaginable field.

biology, and chemistry have brought us to the point where it is becoming possible to begin to understand and utilize self-assembly. Curiously, some of the key developments took place almost contemporaneously with Feynman's lecture. In the 1930's, the British mathematician Alan Turing, developed the theory of universal computation. Long before the arrival of the personal computer, Turing had already liberated computation from the silicon chips with which we so closely associate computation today. With his "Universal Turing Machine," Turing taught us that computation could be thought of abstractly and that all sufficiently complex computers are essentially equivalent. His insight paved the way for Adleman's invention of DNA computing in 1994 and Winfree's 2004 demonstration of computing via self-assembly. In the 1950's the mathematician John von Neumann extended Turing's efforts and developed the theory of automata replication. Von Neumann's work created a framework for future efforts in the development of self-replication, artifical life, and self-assembly. Another key landmark in the history of self-assembly was the discovery of the structure of DNA by Watson and Crick in 1953. DNA, the central molecule of biology, is also of central importance in the study of self-assembly. In addition to being used for computation, it was shown by Nadrian C. Seeman in 1991 that DNA could be induced to self-assemble into mechanical structures. The self-assembled DNA cube of Seeman and Chen has already been improved upon by researchers such as William Shih who has coaxed DNA into self-assembling into octahedra and other complex shapes. Shortly after the discovery of the structure of DNA, Fraenkel-Conrat and

Williams showed that biological systems could be induced to self-assemble in a test tube. There work with the tobacco mosaic virus allowed us to begin to understand how nature uses self-assembly in biology. Another early key development in self-assembly, that occurred shortly after Feynman's lecture, was the invention of "Wang Tiles" by Hao Wang. Wang showed the equivalence of tiling problems and computation, thereby extending Turing's work and providing the second key ingredient for Winfree's demonstration of computation by self-assembly. On the macroscale, other researchers have made fundamental contributions to our understanding and practical implementation of self-assembly. Notable among these is the invention of a simple self-replicating machine by Penrose and Penrose in 1957, the use of surface tension to self-assemble 2-d structures by Hosokawa in 1996, and the practical implementation of surface tension driven self-assembly by Whitesides in 2000. Today, self-assembly is drawing the interest and efforts of researchers from every imaginable discipline. While we are still a long way from duplicating the elegance of nature, we're closer than ever, and getting closer every day.

1.3 Chapter Highlights

- Self-assembly is a multi-disciplinary endeavor. If you want to understand this field and examine self-assembly from a wide variety of perspectives, this book is for you.

- **Self-assembly** refers to the spontaneous formation of organized structures through a stochastic process that involves pre-existing components, is reversible, and can be controlled by proper design of the components, the environment, and the driving force.

- **Static self-assembly** refers to that subclass of self-assembly processes that leads to structures in local or global equilibrium.

- **Dynamic self-assembly** refers to that subclass of self-assembly processes that leads to stable non-equilibrium structures. These structures persist only so long as the system is dissipating energy.

- **Programmed or programmable self-assembly** refers to that subclass of self-assembly processes where the particles of the system carry information about the final desired structure or its function.

- Numerous examples of self-assembling systems may be found in the natural world. These include both organic and inorganic systems. Part I of this text deals with natural self-assembling systems.