Molecular Nanotechnology in Aerospace: 1999

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Abstract

Recent progress towards molecular nanotechnology and potential aerospace applications is reviewed. Great strides have been made in understanding, visualizing, and controlling matter at the atomic scale. In particular, substantial progress has been made towards the construction of molecular computers. Some progress has been made towards understanding biological molecular machines and manipulating these machines for technological purposes. Also, several polymeric molecules, notably proteins, DNA, and RNA, can be automatically synthesized from precise specifications. This example of "programmable matter" has been used to produce at least one molecular mechanical device. However, integration of molecular components into larger atomically precise systems has made little progress. Scaling up molecular nanotechnology to produce macroscopic products of aerospace interest, for example, launch vehicles, will require large research and development investments. In particular, self-replication, proposed as a route to macroscopic molecular nanotechnology products, is a long way from fruition. This paper is a high-level discussion of molecular nanotechnology and some aerospace applications. Applications of importance to aerospace include computers, materials, and sensors. Research reviewed in [Globus 1998a] and [Globus 1998b], for the most part, is not revisited here. Also, this review is not exhaustive and much important and relevant work is not discussed.

Introduction

Molecular nanotechnology, for the purposes of this paper, is the thorough three-dimensional structural control of materials, processes and devices at the atomic scale. The inspiration for molecular nanotechnology comes from Richard P. Feynman’s 1959 visionary talk at Caltech

in which he said, "The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed---a development which I think cannot be avoided." Atomically precise control of matter is progressing rapidly in the laboratory today. A particularly dramatic example was the use of a scanning tunneling microscope to write the characters "IBM" by manipulating xenon atoms on a copper surface [Eigler 1990]. Controlling the fantastic complexity of atomic scale matter will almost certainly require "programmable matter," atomic scale products that are created and/or controlled by computer programs. Current examples include protein, RNA, and DNA synthesis from an exact specification of the sequence. Beyond today's state-of-the-art lie molecular machines, although a few biological molecular machines have been studied, synthesized, and used in laboratory settings. These technologies should suffice for the production of microscopic products. To produce macroscopic objects of aerospace interest will require some mechanism to scale products up in size. Biological systems use reproduction to produce large objects, such as whales and redwood trees, starting with single cells or small seeds. The construction of self-replicating programmable machines, while extraordinarily difficult and dangerous, should enable dramatic improvements in aerospace systems [Globus 1998a].

Any molecular nanotechnology must be based on chemistry, and the field has taken a number of directions. Organic chemists have produced a wide variety of small structures, including testable two junction computer devices [Reed 1998][Rawlett 1999]. Biotechnology has been used to create a wide variety of systems, including 2D crystal patterns of DNA [Winfree 1998], modified copies of biological molecular motors [Montemagno 1999] , and covalently bonded molecular tubes with precise radius [Ghadiri 1993]. Fullerene nanotechnology development has produced transistors [Tans 1998][Martel 1998] and diodes [Collins 1997]. A wide variety of theoretical studies have examined the properties of many other potential devices, including fullerene gears [Han 1997][Srivastava 1997], bearings [Tuzun 1995a][Tuzun 1995a], and three junction electrical devices [Menon 1997].

Progress in molecular nanotechnology can be reasonably expected to enable radical improvement in a wide variety of aerospace systems and applications. Computer technology will probably be the first to feel the molecular nanotechnology revolution, with substantial advantages to the aerospace industry. Theoretical and numerical studies suggest that 10^{18} MIPS computers [Drexler 1992a] and 10^{15} bytes/cm^2 write once memory [Bauschlicher 1997] are possible. It may also be possible to build safe, affordable vertical take-off and landing aircraft to replace personal automobiles [Hall 1999] and eliminate the need for most roads. From [Srivastava 1999b]:

> The development of nanotechnology is important for the exploration and future settlement of space. Current manufacturing technologies limit the reliability, performance, and affordability of aerospace materials, systems, and avionics. Nanotechnology has enormous potential to improve the reliability and performance of aerospace hardware while lowering manufacturing cost. For example, nanostructured materials that are perhaps 100 times lighter than conventional materials of equivalent strength are possible. Embedding nanoscale electromechanical system components into earth-orbiting satellites, planetary probes, and piloted vehicles potentially could reduce the cost of future space programs. The miniaturized sensing and robotic systems would enhance exploration capabilities at significantly reduced cost. Thousands to millions of

such miniaturized devices could help map a planet in a single launch.

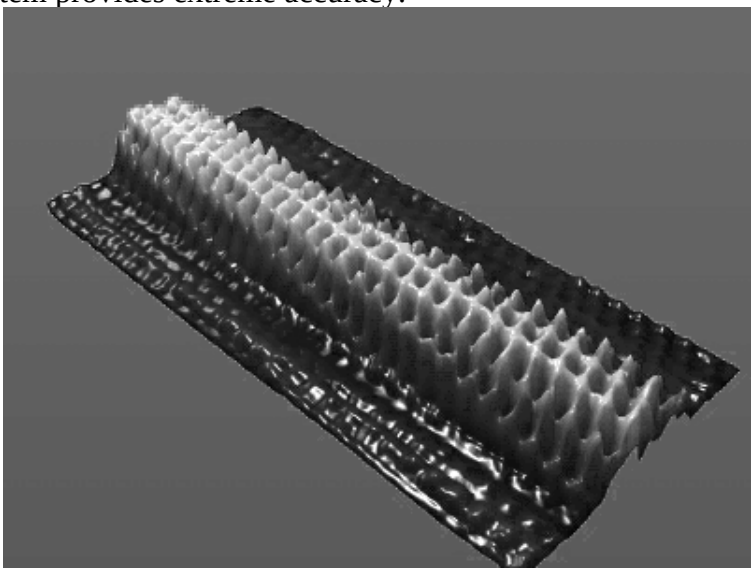
Launch costs might be reduced significantly using molecular nanotechnology. In the extreme case, [Drexler 1992b] estimated that a four passenger single-stage-to-orbit launch vehicle weighing only three tons (including fuel) could be built using a mature diamondoid nanotechnology. More conservatively, [McKendree 1995] estimated $153-412 per kilogram launched to low-Earth-orbit assuming existing single-stage-to-orbit vehicle designs but using diamondoid rather than conventional materials . Current launch costs are many thousands of dollars per kilogram.

The paper is divided into sections reviewing molecular nanotechnology itself (atomic scale control and imaging, programmable matter, molecular machines, and replication), some of the chemistry behind molecular nanotechnology (organic chemistry, biotechnology, and fullerene nanotechnology), and some of the major challenges and opportunities ahead.

Molecular Nanotechnology

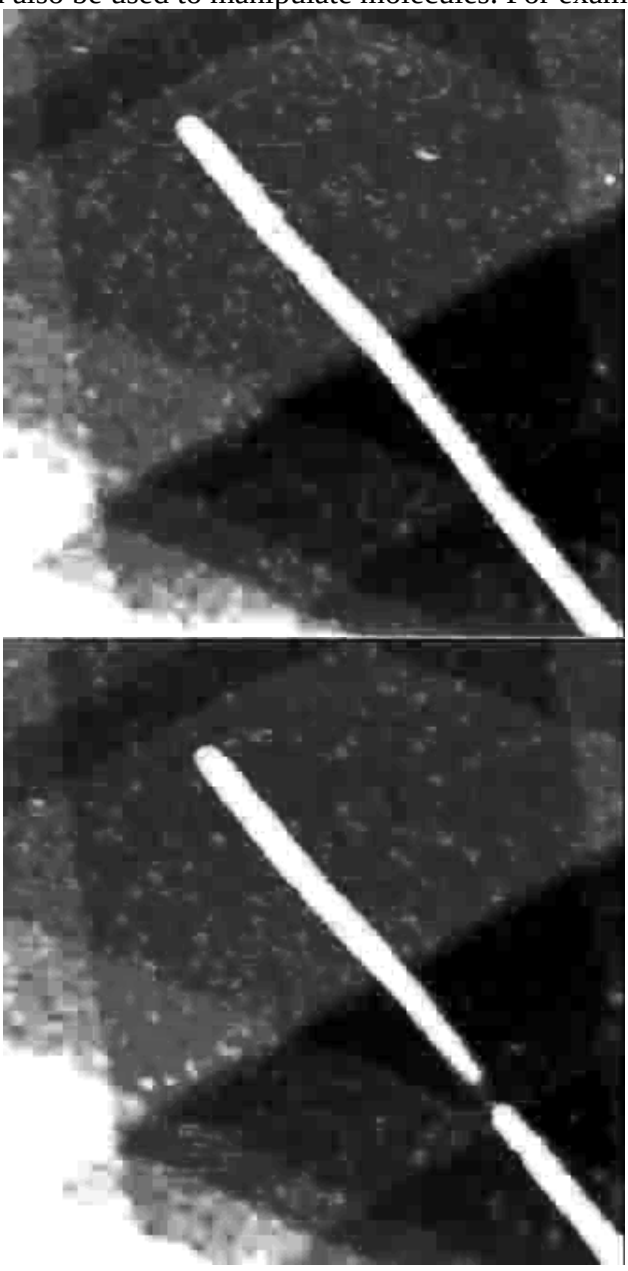
Manipulation and Visualization of Matter at the Atomic Scale

Laboratories throughout the world are rapidly gaining atomically precise control over, and views of, matter at the atomic scale. In particular, scanning probe microscopes (SPM) can image surfaces with sub-atomic precision and manipulate individual atoms [Eigler 1990] and molecules [Gimzewski 1997] on surfaces. Manipulation can be accomplished electronically, mechanically, and/or with chemically active tips. An SPM uses the interaction of a microscopic probe with the surface of a sample to measure characteristics of the sample at localized points. The probe is typically a sharp silicon tip, but can also be other materials, including single walled carbon nanotubes [Dai 1996]. By scanning the sample with a probe in a two-dimensional pattern (like an electron beam scans a television screen), an image can be produced. The motion of the sample is usually controlled by piezoelectric materials, sometimes to sub-atomic accuracy. By measuring the deflection of the cantilever, often with a laser, the interaction is quantified. A feedback loop between controller and the deflection measurement system provides extreme accuracy.



Atomically precise image of a carbon nanotube. Note the helical winding. For small diameter tubes, the helical winding determines the electrical characteristics of the tube. Image due to [Dekker 1999]. Used with permission.

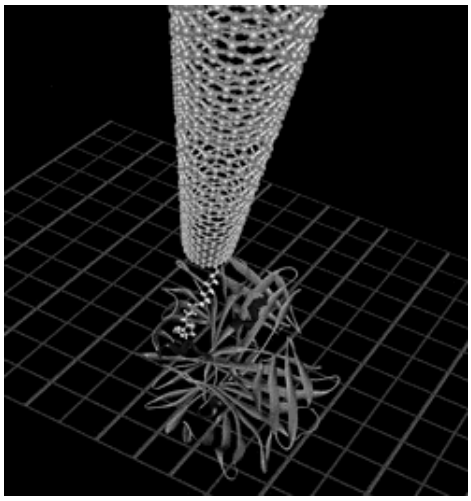
Scanning tunneling microscopy (STM) involves the tunneling of electrons through vacuum from the tip of the STM to the sample. STM is very accurate but can only interact with conductors. STMs can also be used to manipulate molecules. For example:



These carbon nanotubes were cut by applying a voltage pulse to an STM tip. The images show a nanotube before and after cutting. Images due to [Dekker 1999]. Used with permission.

Atomic force microscopes (AFM) usually sense Van der Walls forces from a surface. This allows measurement of nonconductive surfaces as well as operation in air and liquid. If a chemically active molecule is placed on the tip, then an AFM can be used to measure

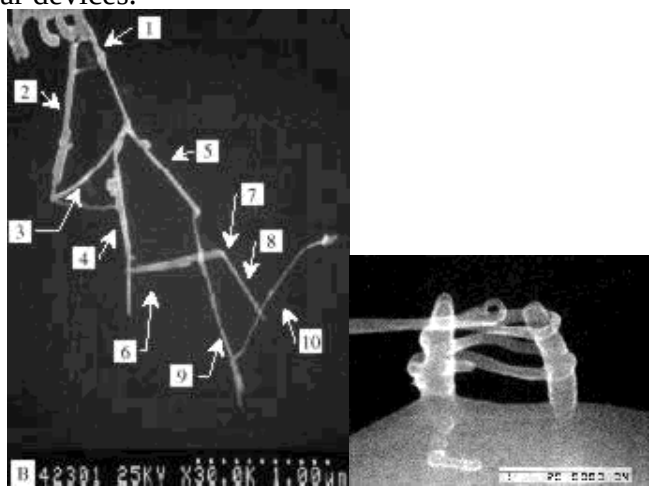
chemical forces between the tip and a surface. [Frisbie 1994] introduced the term "chemical force microscopy" when they coated an AFM tip with a hydrophilic monolayer and imaged a surface patterned with hydrophobic and hydrophilic molecules. While the surface appeared smooth to an unmodified AFM tip, [Frisbie 1994] was able to measure differences in frictional forces between hydrophobic and hydrophilic portions of the surface, achieving an estimated resolution of about 200 nm. To achieve higher resolution, and measure the interaction of individual molecules with a surface, a sharper tip is necessary. [Dai 1996] was able to attach carbon nanotubes to SPM tips to achieve atomic precision. [Wong 1998] subsequently used open ended carbon nanotubes, covalently functionalized with several different molecules, to image a chemically varied surface achieving a lateral chemical resolution of approximately 3 nm, "... significantly better than ... obtained with the use of Si and Si_3N_4 (15 nm) or multi-walled-carbon-nanotube tips (8 nm)" [Wong 1998]. Scanning the sample with different functional groups on the tip resulted in distinctly different images and the differences could be explained on the basis of chemical affinity between the tip and the surface. Since both closed and open carbon nanotubes may be functionalized in many ways, Modified nanotube probes may someday perform extremely well-controlled chemistry at precise locations and use applied forces to overcome reaction barriers.



A model of a carbon nanotube used as a probe with biotin binding to streptavidin. Image from Dr. Lieber's website http://magic.harvard.edu/research.html. Used with permission.

Carbon nanotubes (see the section on Fullerene Nanotechnology below) have been manipulated in several recent studies. [Falvo 1999] was able to demonstrate rolling and sliding of carbon nanotubes pushed by an AFM on mica and graphite surfaces. Stick-slip behavior was observed in the force curves for rolling. [Skidmore 1999] was able to build and observe a variety of carbon nanotube structures by placing multiple SPM tips around a sample within view of scanning and transmission electron microscopes. Electron beam deposition was used to build up structures in localized positions from a gas feedstock. The SPM tips could manipulate the carbon nanotubes and cut them. Three-dimensional structures were built and carbon nanotubes were weaved around posts. [Skidmore 1999] is probably the most sophisticated manipulation of carbon nanotubes to date. The sample and apparatus used for manipulation can be moved from microscope to microscope to take advantage of the

properties of particular devices.



Two artificial nanotube arrangements built by Zyvex, Inc. [Skidmore 1999]. The image on the left shows a nanotube scaffolding. Numbers show the ordering of tube attachment. The image on the right shows nanotube weaving. Images used with permission.

Mechanical manipulation of carbon nanotubes may also lead to a new form of chemistry. [Falvo 1997] was able to repeatedly bend individual multi-walled carbon nanotubes using a interactively-controlled AFM. This manipulation demonstrated the high strength of carbon nanotubes and the formation of kinks when nanotubes are bent. [Srivastava 1999a] computationally predicted that mechanically induced strain leads to regions of enhanced chemical reactivity as carbon atoms change from a stable sp2 (planar) configuration with three neighbors towards a less stable sp3 (pyramidal) configuration with three neighbors and one radical site in regions of greatest strain. [Srivastava 1999a] presents some experimental data that support, but do not confirm, this prediction. If the prediction holds true, mechanical manipulation might be used to induce strain at desired locations along a carbon nanotube leading to selective attachment of functional groups from a reagent bath at those locations.

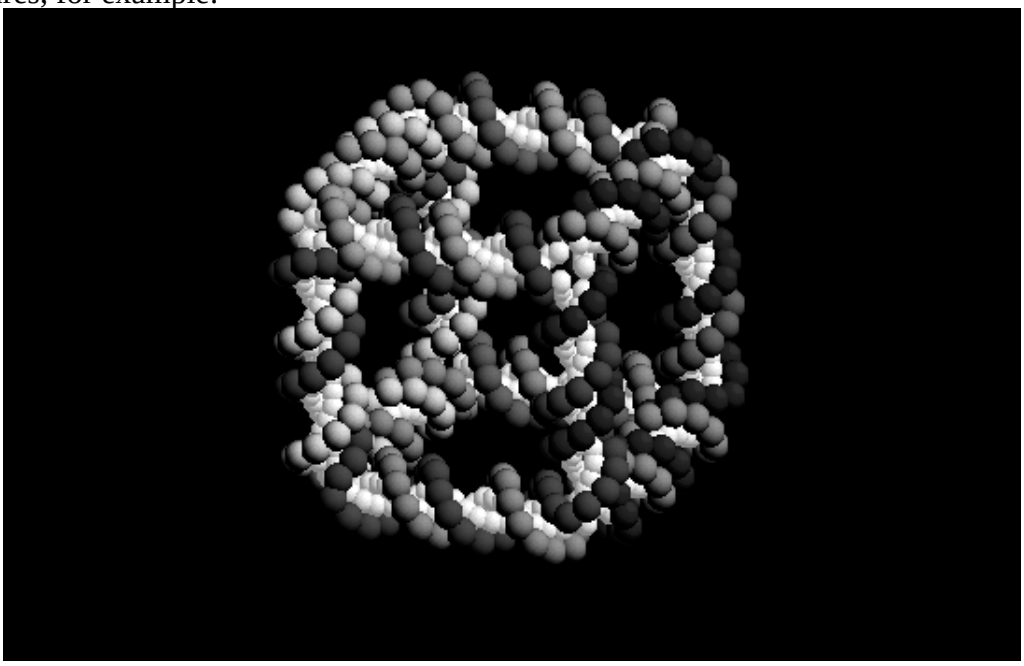
Programmable Matter

Programmable matter refers to the fact that machines exist which, when given the proper instructions and feedstock, will produce physical objects to the given specification. Examples include numerically controlled machines, "fabbers" (available for your PC) which take object descriptions from CAD programs and produce plastic objects of the correct size and shape, and, most important for our purposes, polypeptide, DNA, and RNA sequencers. These sequencers take a specification of the desired sequence of amino acids or nucleotides and produce a sample containing nearly 100 percent of the desired molecules. The cost as of September 1999 is about $1-10 per base (amino acid or nucleotide) in the sequence (source: the back page of *Science*, any issue in the last few years).

In a spectacular example of the power of programmable matter, [Schwarze 1999] use a portion of the HIV viral protein to insert a wide variety of proteins into mammalian cells and live mice. Typically, only small therapeutic molecules can enter cells. [Schwarze 1999] attached an 11 amino acid protein transaction domain from the HIV virus to a variety of proteins. The protein transaction domain apparently enters cells directly through the lipid bilayer component of the cell membrane, not through special pathways. The desired proteins

were denatured (unfolded), attached to the transaction domain, and then passed into the cell where the cell's protein folding machinery folded the protein into a potentially active form. Since essentially any polypeptide can be made by sending the sequence specification and a credit card number to any of several companies, it may be possible to engineer proteins to attack specific points in the molecular life-cycle of disease organisms and deliver these proteins into infected cells. With a polypeptide sequencer and related biotech systems on-board a space station, when disease strikes the necessary medicine for that particular pathogen could be manufactured on-board from instructions sent up from the ground. This would reduce the need for large stocks of medicine for every possible contingency. The same protein sequencer could also be used for research purposes.

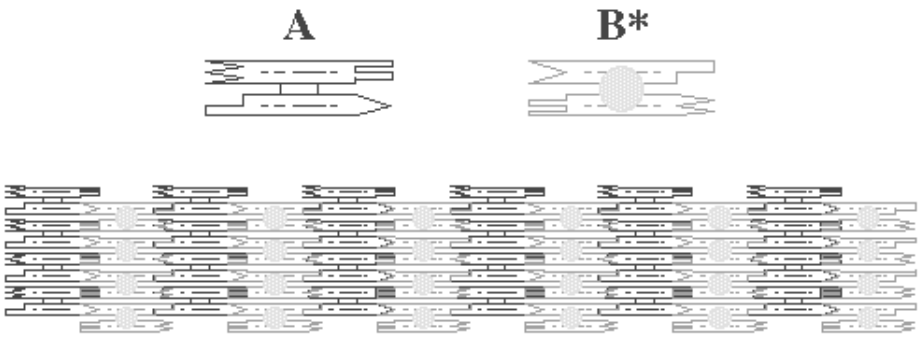
DNA has been used to build 3d topological shapes [Chen 1991][Zhang 1994], stiff structures [Li 1996], crystals [Winfree 1998], and even a molecular machine [Mao 1999a]. This was accomplished by taking advantage of DNA's hydrogen-bonded complementarity and biotechnology's ability to produce almost any DNA sequence desired. By cleverly choosing the sequence of base pairs, Seaman's laboratory has produced a remarkable variety of structures, for example:



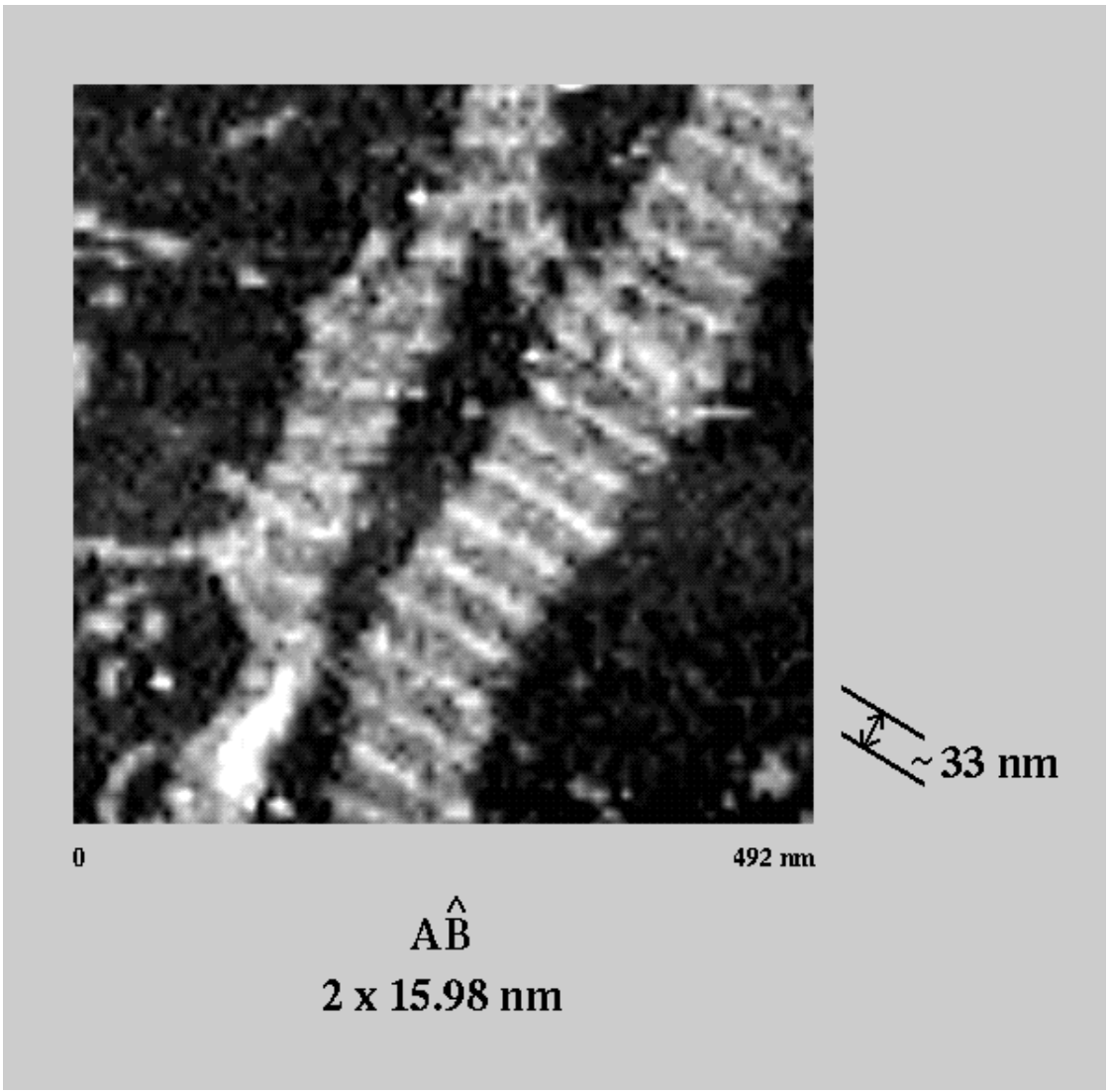
DNA cube made from six different cyclic strands. The DNA backbones are shown in different colors. Each nucleotide is represented by a single colored dot for the backbone and a single white dot for the base. To get a feeling for the molecule, follow the red strand around its cycle. Each edge of the cube is a piece of double helical DNA containing two turns of the double helix. Image due to Ned Seeman [Chen 1991] and http://seemanlab4.chem.nyu.edu/nano-cube.html. Used with permission.

The image notwithstanding, these cubic molecules are not stiff. In other words, the complexes are topological cubes but not geometric cubes. To create stiff molecules, a more complex scheme is necessary. One approach is to use double crossover DNA strands [Li 1996]. Double crossover DNA complexes are multiple strands of DNA that cross over each other in a variety of patterns and some patterns form stiff structures. These strands can be formed into crystals by taking advantage of the single DNA strands on the edge of the

double crossover molecule (the "sticky ends") [Winfree 1998]. For example:



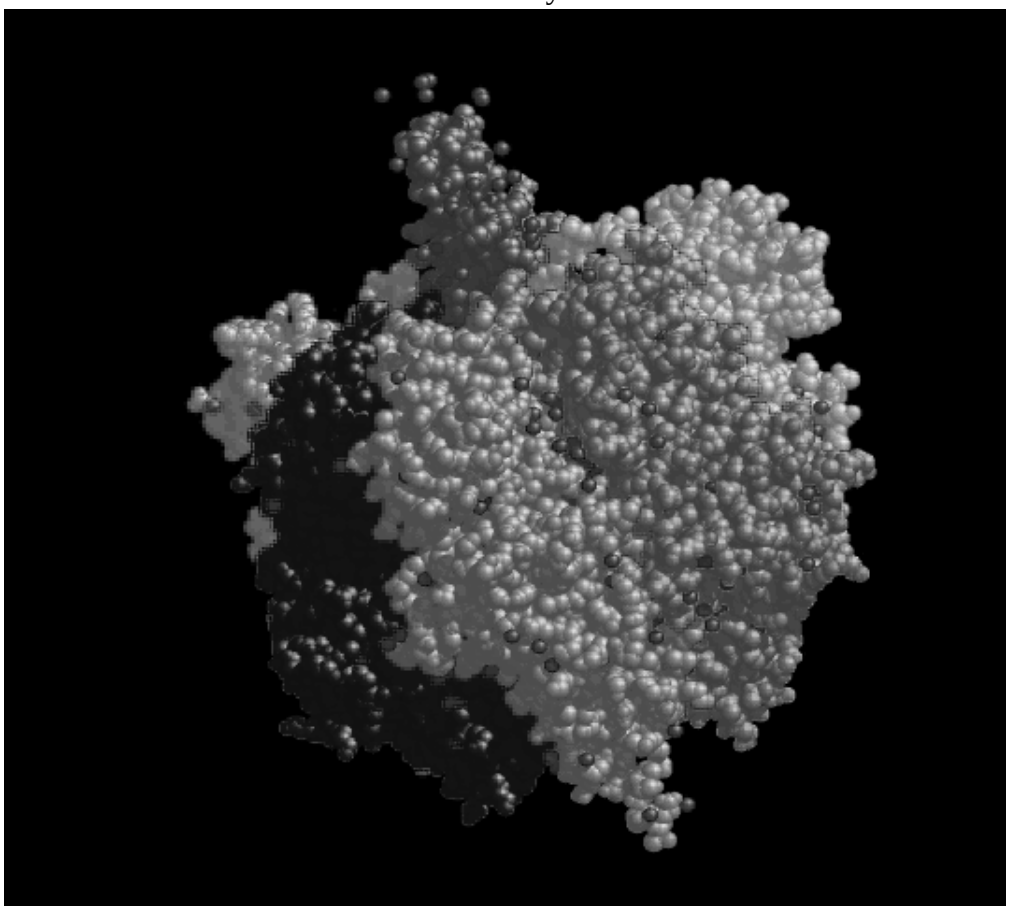
Two DNA double crossover molecules A and B* use complementarity between their sticky ends (represented as geometric complementarity) to form a two dimensional crystal. The B* molecules contain DNA hairpins that project out of plane to allow AFM discrimination. The molecules are approximately 4 nm wide, 16 nm long and 2 nm thick. When these tiles are mixed in solution, they form hydrgen bonded 2-D arrays several microns long and hundreds of nanometers wide. The rows of hairpins appear as stripes separated by ~32 nm when imaged by AFM (below) [Mao 1999b]. Images due to Ned Seeman from http://seemanlab4.chem.nyu.edu/two.d.html. Used with permission.



Molecular Machines

Much of the promise of nanotechnology for aerospace applications comes from the theoretical abilities of atomically-precise molecular machines [Drexler 1992a]. While SPMs provide positional control at the atomic scale, they are too bulky to build macroscopic products atom by atom because the parallelism is limited by the size of the machines. However, very large numbers of molecular machines can fit in a small space and, properly organized, could provide the parallelism necessary to build macroscopic products by positioning individual atoms. To date, only one such machine has been built, although several computational studies have been undertaken [Tuzun 1995a][Tuzun 1995b][Han 1997] [Srivastava 1997][Cagin 1998]. [Gimzewski 1998] observed a molecular rotor operating on an atomically precise copper surface in ultrahigh vacuum. The molecule rotated due to thermal energy when separated from a bearing formed by a hexagonal lattice of the same molecules. Rotation stopped when the molecule moved into contact with the hexagonal lattice. However, living cells abound in much more sophisticated molecular machinery built primarily from proteins. Some of these machines have been isolated, modified and studied.

[Montemagno 1999], building on the work of [Noji 1997], is attempting to integrate the biological motor F_1-ATPase with nano-electro-mechanical systems to create a new class of hybrid nanomechanical devices. ATPase is used by mitochondria to synthesize ATP from ADP, phosphate, and proton gradients. ATP is the primary energy source of our bodies. The F1 portion of ATPase has a sub-unit that turns during synthesis. This rotation can be reversed by separating the F1 sub-unit from the rest of the protein and feeding the sub-unit ATP. F_1-ATPase can generate >100 pN, has a measured rotational velocity of 3 r.p.s. under load, and a diameter of less than 12 nm. These characteristics suggest that F_1-ATPase could manipulate currently manufacturable nanomechanical structures. Since the human body produces ample quantities of ATP, an implantable sensor in an astronaut's body operated by F_1-ATPase would require no other power source. Such sensors could provide medically important data on an astronaut's health indefinitely.



F_1-ATPase [Abrahams 1994]. The orange sub-unit rotates. The six sub-units in shades of yellow, green and blue rock back and forth sequentially as ATP is hydrolyzed [Elston 1998].

Another biological molecular motor, kinesin, was deposited on polymer films in order to guide the motion of microtubules on surfaces [Dennis 1999]. Kinesin has also been used to manipulate 10 x 10 x 5 μm silicon microchips. These microchips were translated, rotated, and in a few instances turned over by large numbers of kinesin motors [Limberis 1999]. Normally, kinesin motors operate on microtubule "tracks" inside cells. From [Limberis 1999]:

> The microtubule tracks are hollow tubes, 24 nm in diameter, formed by the self-assembly of tubulin protein subunits. The engines of this transport system, kinesins, are remarkable molecular machines. Force production is coupled to hydrolysis of ATP, a high-energy biomolecule. For each ATP it hydrolyzes, kinesin steps 8 nm [Svoboda 1993] on the microtubule surface and can generate forces up to 6 pN ... [Hunt 1994]. With a cross-sectional area on the order of 10 nm^2 [Kull 1996], kinesin can be surface immobilized with a packing density approaching 10^5 motors per μm^2. With each motor generating forces as high as 6 pN, cumulative forces on the order of 10s of nN per μm^2 are theoretically possible.

In an attempt to understand the conditions under which kinesin fixed to a surface could move microtubules, [Unger 1999] demonstrated that kinesin-driven microtubules can work continuously up to several hours. They can operate on uneven surfaces with height differences up to 280 nm and in chambers as small as about 100 nm. The height difference was determined by using polished silicon wafers into which steps were etched. The wafers were covered with kinesin. When microtubules were added to a solution on the slide, they were observed (with an optical microscope) gliding across the wafer surface. To determine chamber size, microtubules gliding between two glass slides were investigated. Microtubules were transferred to a kinesin-coated glass slide. To produce variable heights, a slightly curved coverslip was used. An interferometer was used to measure the distance between slides.

[Mao 1999a] created an artificial two-state molecular machine from DNA. [Mao 1999b] connected two stiff double-crossover DNA molecules [Li 1996] with a strand of DNA that could assume either a right-handed helix (B-DNA) or a left-handed helix (Z-DNA) conformation depending on certain characteristics of the solution the molecules were in. By changing the solution and forcing the connecting DNA strand to wind in the opposite direction, the stiff portions were forced to move. This movement was recorded by placing dye molecules on each stiff segment. "The switching event induces atomic displacements of 20-60 angstroms" [Li 1996]. This experiment was controlled by running the same test on similar DNA molecules where the connecting segment was not capable (due to the sequence used) of assuming the Z-DNA conformation. These molecules did not change conformation when the solution changed.

A very interesting non-biological partly-molecular machine has been fabricated by Philip Kim and Charles M. Lieber [Kim 1999]. They attached a nanotube bundle to each of two independent electrodes deposited on a pulled glass micropipette. This enables independent control of charge on each nanotube. When the nanotubes are oppositely charged they can be induced to close like tweezers - nanotweezers - thereby enabling nanoscale objects to be held and manipulated in three dimensions. The nanotube nanotweezers have been used to manipulate and measure the electrical properties of nanoclusters and nanowires.

Replication

While molecular nanotechnology is making great strides with respect to very small products, many aerospace applications, particularly placing and maintaining humans in orbit, require

macroscopic systems. This requires integration of vast numbers of microscopic elements. Biological systems scale up from very small beginnings by cell replication. Thus, some nanotechnology pioneers have proposed building programmable molecular machines capable of self-replication [Drexler 1992a]. These hypothetical machines are often called assemblers. Theory suggests that self-replicating assemblers could lead to fantastic productivity because of their exponential growth potential. Although molecular-scale assemblers have garnered substantial attention, the most detailed study of artificial self-replication was a 1980 NASA summer study that assumed macroscopic machines [Freitas 1980].

[Freitas 1980] studied a hypothetical 100-ton self-replicating lunar factory with access only to local resources and established materials processing techniques. This study assumed macroscopic machines, not nanotechnology. While a number of self-replication strategies are possible, perhaps the most practical is for a computer to interpret a set of instructions and control a robot to make a copy of itself, a technique originally proposed by von Neuman. This has the added virtue that the instructions can be changed so the replicator can make something else. If the computers themselves are provided using mass production technologies instead of replication, then the replication can be limited and controlled to avoid the most serious runaway scenarios.

From [Freitas 1980]:

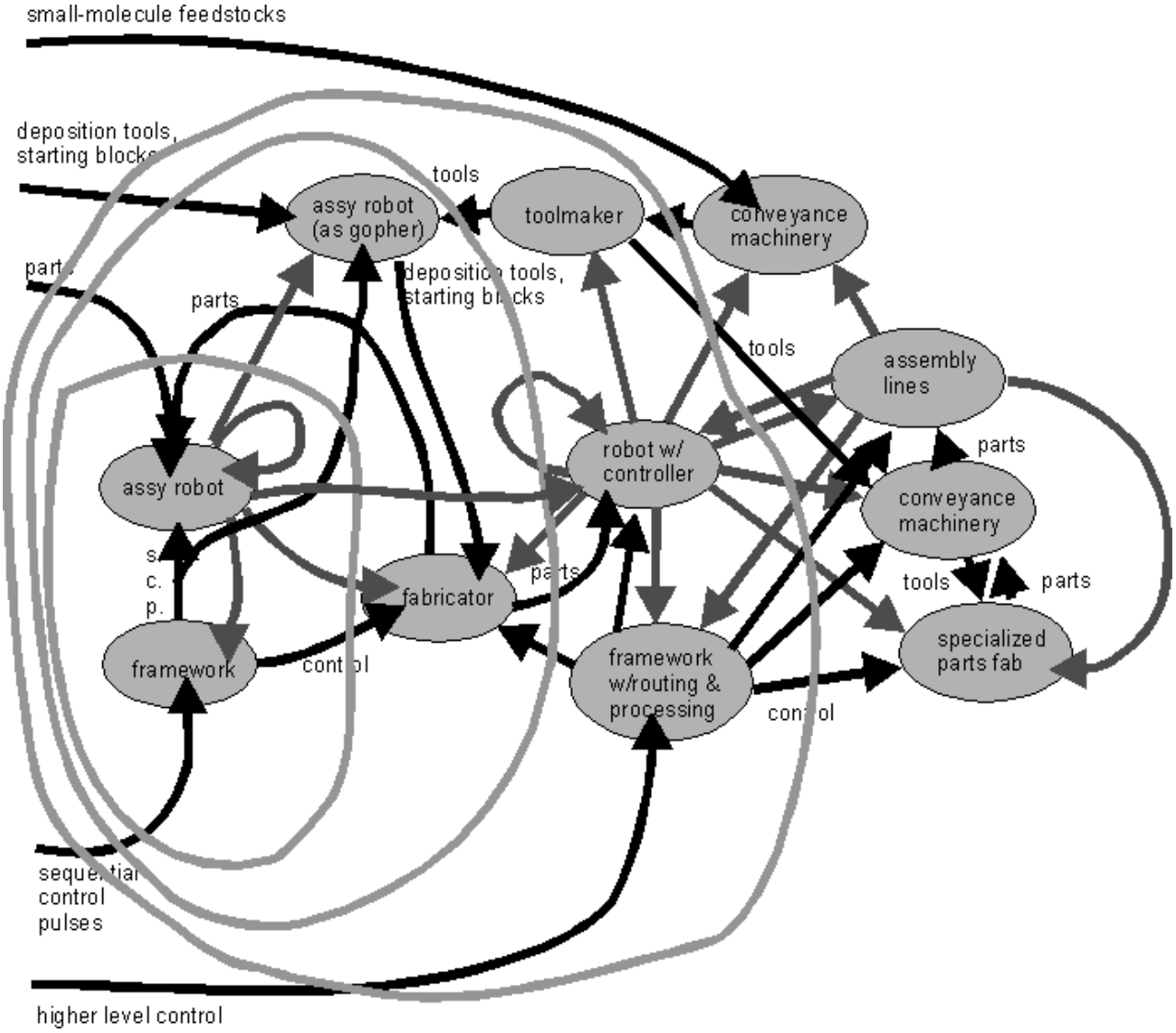
> The Replicating Systems Concepts Team reached the following conclusions concerning the theory of machine reproduction:
>
> - John von Neumann and a large number of other researchers in theoretical computer science following him have shown that there are numerous alternative strategies by which a machine system can duplicate itself.
> - There is a large repertoire of theoretical computer science results showing how machine systems may simulate machine systems (including themselves), construct machine systems (including machine systems similar to or identical with themselves), inspect machine systems (including themselves), and repair machine systems (including, to some extent, themselves). This repertoire of possible capabilities may be useful in the design and construction of replicating machines or factories in space.
>
> It is interesting to note that computer programs capable of self-replication have been written in many different programming languages [Burger 1980][Hay 1980], and that simple physical machines able to replicate themselves in highly specialized environments have already been designed and constructed [Jacobson 1958][Morowitz 1959][Penrose 1959].

[Hall 1998] developed a simple analytical model to describe the performance of self-replicating machines. This model describes a system "... composed of a population of replicating machines. Each machine consists of control and one or more operating units capable of doing primitive assembly operations (e.g. mechanochemical deposition reactions). Let us define the following:

p(t) -- population at time t

g -- generation time (seconds to replicate)
a -- "alacrity" primitive assembly operations per second
s -- size in primitive operations to construct
n -- number of primitive operating units

Then $g = \frac{s}{na}$ and $p(t) = \left\lfloor 2^{\frac{t}{g}} \right\rfloor$." [Hall 1998] then investigated the implications of such a model, particularly with regards to bootstrapping ever more capable replicators. From this analysis, he derived a potential system architecture detailed in the following figure:



"System diagram for the bootstrap path of a self-replicating manufacturing system. Each subsystem in a blue line (as well as the entire system) meets the self-replicating system criterion." The turquoise ellipses represent components. The black arrows represent material or information flows. The red arrows represent fabrication. By Hall's criteria, a system is self-replicating if every turquoise ellipse has an incoming red arrow and all red arrows originate from a turquoise ellipse. Image from [Hall 1998]. Used with permission.

[Hall 1998] also proposed using the term replication to describe machines producing exact copies of themselves and distinguishing this from biological reproduction which implies evolution of species. These conventions are used in this paper, although not in all of the quotes.

[Freitas 1980] suggested several applications for space based self-replicating manufacturing systems (SRS). Such systems might use solar energy and lunar or asteroidal materials. Asteroidal materials might be delivered by large numbers of fully automated solar sail powered spacecraft that capture and return small (~1 m diameter) meteoroids [Globus 1999]. From [Freitas 1980] :

> Manufacturing. Huge solar power satellites with dimensions 1-10 km on a side could be constructed in Earth orbit by a fleet of free-flying assembly robots or teleoperators manufactured by a replicating factory complex using material from the Moon. Components for very large structures, including communications, storage, recreational, penal, or even military platforms could be fabricated, and later assembled, by an SRS. Another exciting mass-production possibility is the notion of orbital habitats, or "space colonies" [O'Neill 1977][O'Neill 1979], by which increasingly large populations of human beings could be safely and comfortably maintained .... Additionally, a replicating factory could build more copies of itself, or new variants of itself capable of manifesting different behaviors and producing different outputs, in almost any desired location...
>
> Observation. Exceedingly large sensor arrays for Earth or astronomical observations could be rapidly constructed from nonterrestrial materials by a self-replicating manufacturing facility. This technology could be used to make feasible such advanced missions as optical extrasolar planet imaging (using millions of stationkeeping mirror assemblies arranged in an array with an aperture diameter on the order of kilometers); complex multisensor arrays; very large, high-resolution x-ray telescopy; and other self-organizing optical or radio telescopic arrays of grand proportions to permit such ambitious undertakings as galactic core mapping, continuous observation of large numbers of passive fiducial markers for Earth crustal plate motion monitoring, and various SETI (Search for Extraterrestrial Intelligence) observations including beacon acquisition, radio "eavesdropping," or, ultimately, active communication. Automated mass production will make possible arrays with heretofore unattainable sensitivity and spatial resolution.
>
> Experimentation. Replicative automation technology will permit a tremendous expansion of the concept of a "laboratory" to include the Earth-Moon system and ultimately all of the bodies and fields in the Solar System. A number of grand experiments could be undertaken which would prove too costly if attempted by any other means. For example, an Earth orbital cyclotron could be constructed as a series of thousands of robot-controlled focusing coils and stationkeeping target assemblies within the terrestrial magnetosphere, with operating energies possibly as high as TeV for electrons and GeV for protons. Additional experiments on magnetospheric propulsion and energy generation could be conducted by free-flying robot drones manufactured on and launched en masse from the lunar surface. Gravity field probes, including mascon mappers and drag-free satellites, could be coordinated to perform

complex experiments in kinematics, special and general relativity, and celestial mechanics.

The construction of artificial molecular self-replicating systems is in its infancy. In a state-of-the-art study, [Lee 1996] demonstrated the operation of a self-replicating 32-residue peptide based on a yeast protein. This peptide acts autocatalytically in a solution of appropriate 15- and 17-residue fragments that combine to form the 32-residue peptide.

Any technology employing replicators will require mechanisms to insure safe use. Existing replicators such as bacteria and viruses cause severe problems; for example, human death rates exceeding 50 percent in unprotected populations. The possibility of accidental or deliberate misuse of replicators must be addressed, preferably before problems arise. One threat is the production and release of artificial infectious agents, an extension of the germ warfare in development today. Current efforts to address germ warfare defense could be extended to address artificial threats. Control approaches include only designing replicators that require crucial components to be built by other means, not allowing replicators to program themselves, and only developing replicators that function solely in artificial environments, such as a helium atmosphere. A second threat is the rapid production of large quantities of armaments using the exponential growth capability of replicators. Continuous, high resolution, and ubiquitous monitoring may be required to meet this threat. Unfortunately, it may be possible to develop dangerous replicators in great secrecy. Note that the Iraqi government hid their germ warfare program from onsite inspection for years until a defector blew the whistle. Thus, it is probably extremely important to develop molecular nanotechnology out in the open with universal access to results. Requiring free publication of at least government funded results on the World Wide Web is one strategy. Many molecular nanotechnology scientists follow this practice today.

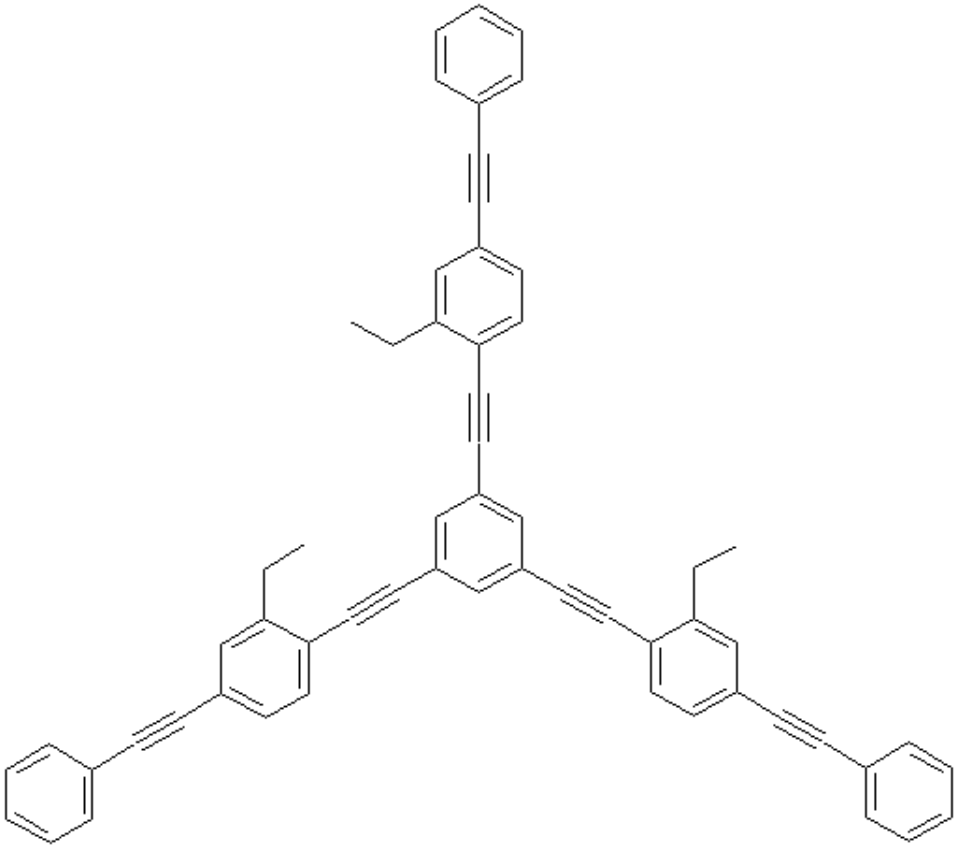
Chemistry

Organic Chemistry

For over a century, organic chemists have been developing ever more sophisticated techniques to construct specific molecules in huge quantities. For organic chemists, these molecules involve carbon, by definition and because of carbon’s uniquely flexible chemistry which allows linear, planar, and tetrahedral constructs. Although the individual molecules are, by definition, atomically precise, the collections of molecules produced by chemists are generally poorly ordered. Still, as chemists scale up to building larger and larger molecules, and still larger aggregates using self-assembly, the potential for organic chemists to contribute to the development of molecular nanotechnology is difficult to overestimate. Self-assembly refers to the process of forming larger, atomically precise aggregates by careful control of inter-molecular forces. In this section we examine only an infinitesimal fraction of the organic chemistry work relevant to nanotechnology. In particular, we examine attempts to construct computer components using organic chemistry.

[Tour 1998] synthesized a number of organic molecules based on benzene and investigated their computational possibilities. Since these molecules can be controllably synthesized in

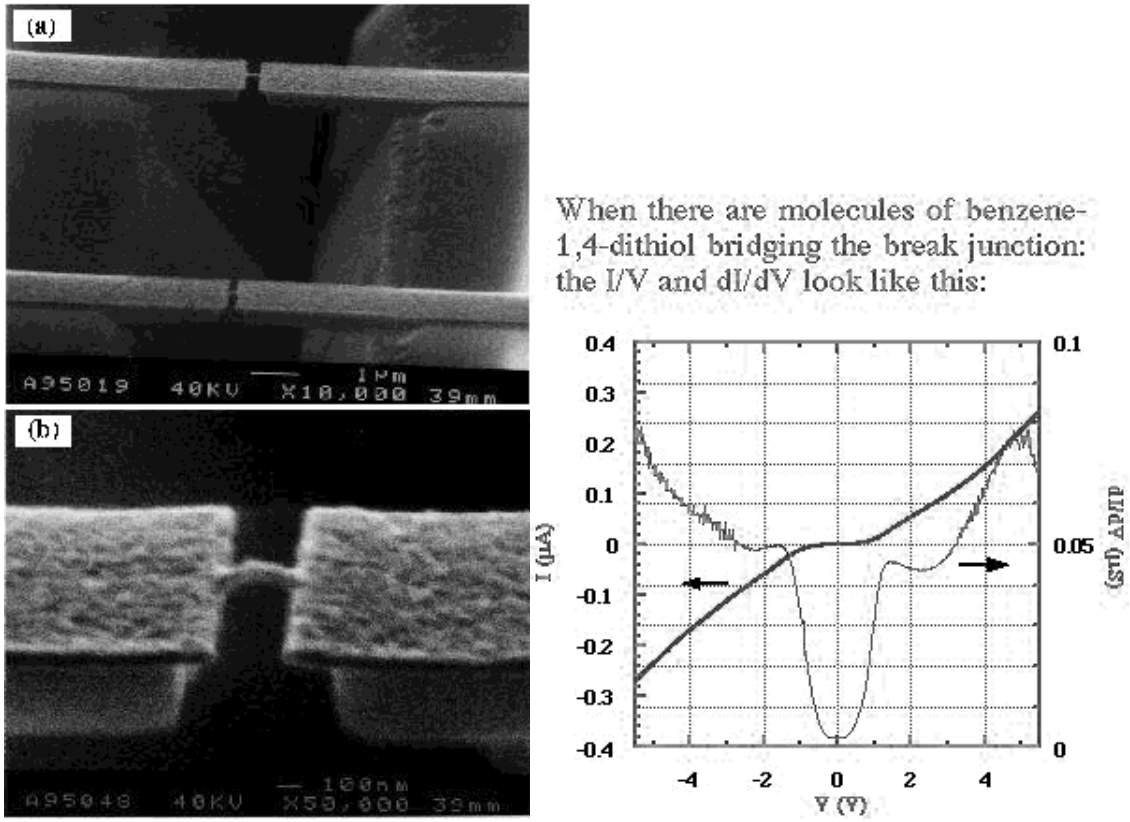
vast numbers, they have great potential as building blocks for nanoelectronic circuits. Noting that transporting electrons through networks of such molecules would generate unacceptable amounts of heat, [Tour 1998] proposed using small changes in electron density to pass information and perform logic functions. While [Tour 1998] discussed quantum calculations to support the notion of using electron density changes for logic, it's unclear how the small signals proposed could be distinguished from thermal noise [Bauschlicher 1999], an issue not addressed in [Tour 1998]. Nonetheless, if these molecules can be connected appropriately, noise problems overcome, and a variety of other problems conquered, these molecules could lead to molecular computers operating at femtosecond time scales.



Three junction device from [Tour 1998].

[Reed 1998] devised a novel mechanically controllable break junction to staticly test benzene-1,4-dithiol molecules, a component of the devices in [Tour 1998]. Using this device, [Reed 1998] was able to reproducibly measure the conductance of single molecules. The observed resistance, approximately 22 Mohm and 13 Mohm depending on the bias, was within the error bounds derived from measurements on an ensemble of similar molecules.

Micromachined Break Junction



Images used with permission [Reed 1998].

[Reed 1998] also built a device to directly measure the conduction through a small group of organic molecules using self-assembly and semiconductor fabrication techniques. This device was used to measure a diode-like molecule:

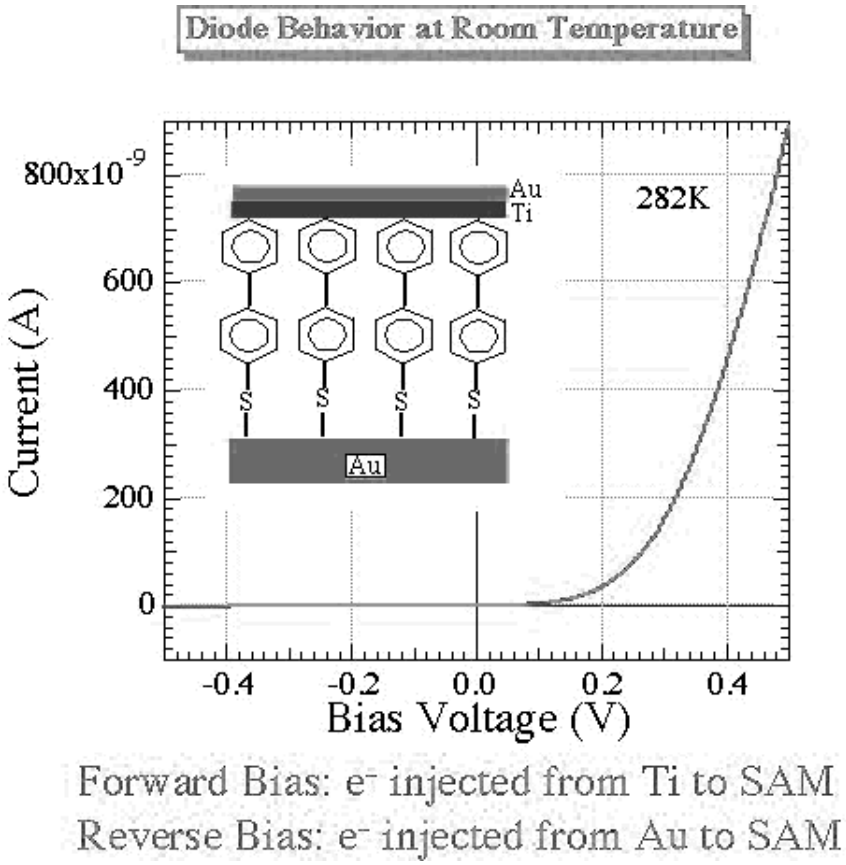
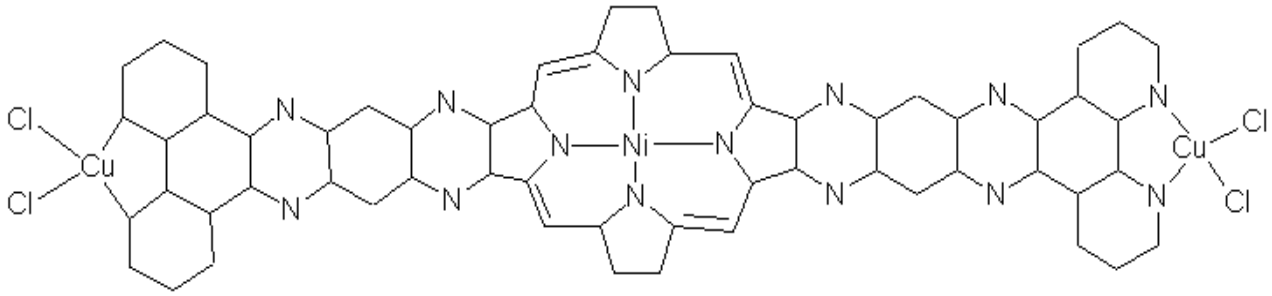


Image used with permission [Reed 1998]. SAM stands for self-assembled monolayer, i.e., a layer exactly one molecule thick.

[Ellenbogen 1999] designed a one bit adder out of molecular wires [Tour 1998] with chemical groups added to implement molecular resonant tunneling diodes and molecular rectifying diodes. These two diodes are sufficient to implement AND, OR and XOR logic elements. In turn, these logic elements are sufficient to implement a wide variety of devices, including adders. The full adder would occupy approximately 25 nm by 25 nm of a surface, approximately one million times smaller than current electronics. However, such a circuit has no gain and probably would not work well in an extended system. There is also reason to believe that the clock rate of these molecular devices would be quite low, possibly slower than current electronics. Quantum calculations suggest that each component of the adder would work properly, but the entire adder may or may not work due to coupling between the devices. Nonetheless, [Ellenbogen 1999] is a substantial step towards molecular electronics.

One problem with these molecular electronics devices is the low levels of current measured experimentally [Reed 1998]. However, [Emberly 1998] used computation to suggest that the low levels of current are due to the contact with the gold leads, not the molecule itself. In fact, molecular wires modeled with strong coupling to the leads were found to have currents orders of magnitude better than observed experimentally. Molecular wire current computed assuming weak coupling matched experiment [Emberly 1998]. If these computations turn out to reflect reality, then a different choice of contacts may lead to higher currents and more practical computer components based on organic chemistry.

Another problem with the molecules discussed so far is that they contain no fused rings and are thus fairly floppy. [Hush 1998] proposed using porphyrin chemistry with fused ring connectors for molecular electronics.



Porphyrin-based molecule with metal contacts at ends.

[Hush 1998] noted that any molecular family used for molecular electronics should have several properties, including:

1. Synthesizability. Porphyrin synthesis is well-established and it is reasonable to expect that synthetic problems can be solved. Oligoporphyrin molecules approximately 12 nm long have been synthesized and longer molecules should be possible.
2. Stability. Porphyrin is the basis of many important biological molecules and can survive in the harsh environment of a body for at least a few days.
3. Synthetic flexibility. Over 100 different oligoporphyrins have been synthesized.
4. Solubility. This is required for chemical manipulation. The solubility of oligoporphyrins can be readily modified.
5. Rigidity. The fused ring structure of oligoporphyrins is much stiffer than the molecules proposed in [Tour 1998]. Carbon nanotubes are stiffer still. These are discussed in the section on fullerene nanotechnology below.
6. Self-assembly. Self-assembly may be essential for large-scale rapid construction of complete systems. Preliminary studies have suggested that oligoporphyrins systems can self-assemble.
7. Attachment. The metal ends that can be attached to oligoporphyrins should provide ready coupling to larger devices for input and output.
8. Junctions. Oligoporphyrins are two-dimensional molecules that have four attachment points 90 degrees apart allowing large molecules to form grid-like structures. The metals in the porphyrin may provide a mechanism for out-of-plane attachment allowing layer-by-layer assembly of three-dimensional devices.
9. Functionality. There is reason to believe that oligoporphyrins can transmit information over long distances via superexchange effects. However, this has not yet been demonstrated experimentally [Hush 1999].
10. Rectification. Rectification has not yet been demonstrated in oligoporphyrins, but the strategy used by [Ellenbogen 1999] should be effective.
11. Switching. [Hush 1998] investigated slow switching using chemical means and provided supporting computational results.

[Heath 1998] built a computer (the Teramac) from a large 2D grid of wires connected by switches. By design, the Teramac had many faulty components and was not initially hard

wired as a computer. A conventional computer used sophisticated software to identify faults and configure the Teramac into a correctly functioning computer. This represents a significantly different architecture than most computers in use today. The fault tolerance and regular structure is significant for molecular computers because regular structures with numerous faults are routinely built from a wide variety of molecules. [Collier 1999] took a step towards building a molecular scale Teramac-like computer using rotaxane molecules as switches under ambient conditions when they:

> "... developed an electronically (singly) configurable junction that consists of a molecular monolayer and a tunneling barrier sandwiched between lithographically fabricated metal wires ... We demonstrate that this junction can be used as a switch, and that several devices, fabricated in a linear array structure, could be used as electronically configurable wired-logic gates (an AND and an OR gate). Because these switches are only singly configurable, they cannot be used for random access memory (RAM) applications, although programmable read only memory (PROM) applications are possible. However, they do have several advantages. First, and most importantly, they should scale down to molecular dimensions without appreciable loss of performance ... Second, when the molecular switches are closed, current flows by resonant tunneling into the molecular electronic states. The net result of this resonant tunneling is that the high and low current levels of the logic gate truth tables are widely separated. This should lead to good noise immunity in future logic circuits built with this technology. Third, molecular switches are voltage addressable rather than field addressable. This makes the device robust with respect to dimensional tolerances in manufacturing. In a CMOS-based configurable device ..., two wires (address lines) are used to configure the switch, whereas two different wires (data lines) are used to read it. For our junctions, only two wires are necessary to achieve both functions. One voltage is applied to read the device, and a voltage of opposite polarity is applied to configure it. The configuration voltage of our devices can be a factor of two greater than the logic levels used when they are operating. This means that it should be easy to design circuits that are safe from accidental reconfiguration under operation conditions. Finally, this architecture is highly modular. We report here on the properties of three different molecular switches incorporated into sandwich devices composed of various combinations of metallic wires." [Collier 1999]

We see that at least three approaches using organic chemistry may lead to molecular computers. While organic chemists have been making functional molecules for over a century, biological systems have made much more capable molecules for over three billion years.

Biotechnology

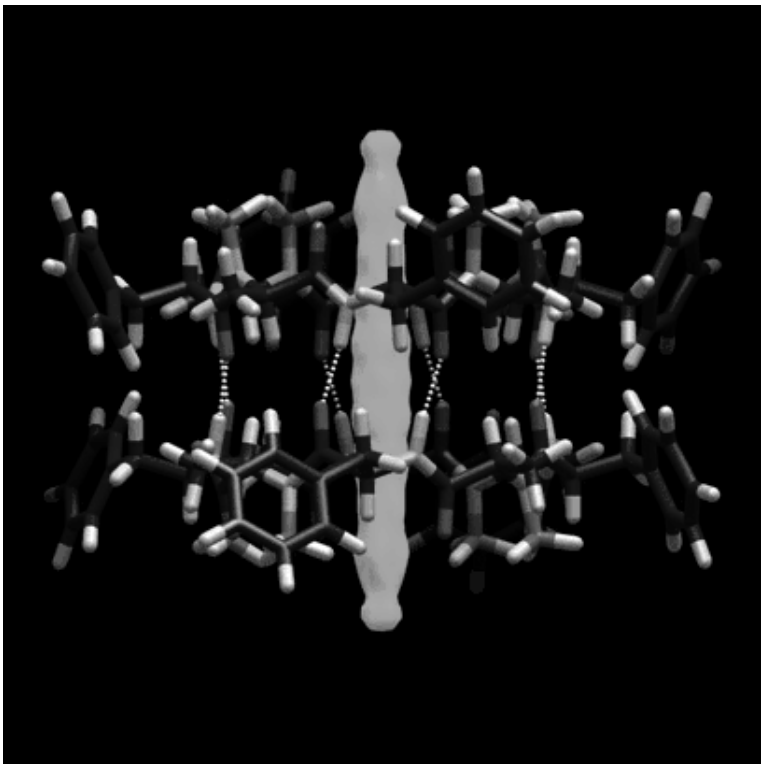
The argument for biotechnology applications to molecular nanotechnology was beautifully made by [Hartgerink 1996]:

> Traditionally microscopic devices have been made by being cut or formed from larger objects, but as these products shrink below the micron level this process becomes increasingly difficult. Recently chemists have begun to try the opposite approach, that is, building these nanoscale objects from molecular building blocks. Although these

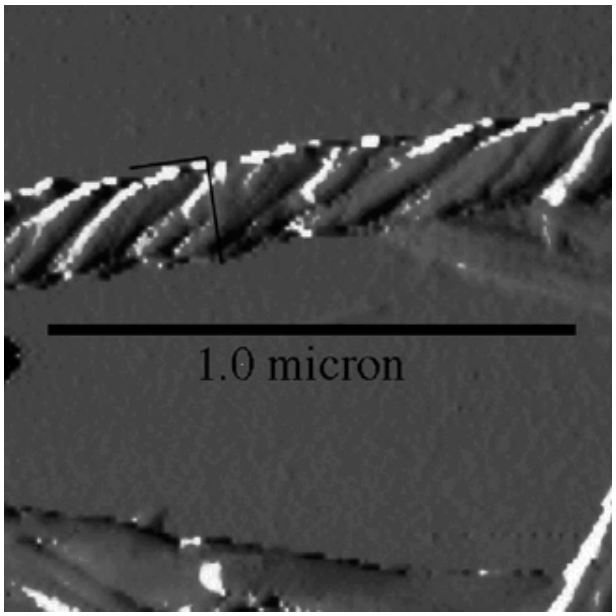
devices are too small to be manufactured by traditional materials science approaches, they are also far too large to be synthesized by classical chemical synthesis. In order to reach these nanoscale devices from a molecular level up, a massively convergent synthesis is required. Production of these nanoscale objects is not, however, unknown and has been occurring for over three billion years -- in living, biological systems. From microtubules to viruses, nature has used a broad variety of self-assembly techniques to build its sub-cellular machines that ultimately lead to life.

In a series of papers starting with [Ghadiri 1993], a wide variety of nanotubes were constructed from artificial cyclic peptides. A peptide is a short sequence of amino acids. The nanotubes have adjustable pore sizes, easily modified surface chemistries, open ends for packing metals or passing ions and small molecules, and are relatively easily synthesized by combining peptide synthesis with self-assembly. From [Hartgerink 1996]:

> Our approach uses cyclic peptides with an even number of alternating D and L amino acids for the building blocks of the nanotubes. The alternating stereo chemistry of the cyclic peptides allows them to sample an open, flat conformation in solution which allows all the side chains of the amino acids to be pointing outwards which would not be possible in an ordinary all L cyclic peptide. In this conformation, the amide backbone is able to hydrogen bond in a direction perpendicular to the plane of the cyclic peptide. When two cyclic peptides stack upon one another the hydrogen bonding network that is formed is like an anti-parallel b sheet , which is commonly found in natural proteins. As this hydrogen bonding lattice propagates perpendicular to the plane of the cyclic peptide a tubular structure is formed.



"Crystal structure of cyclo-[(L-Phe-D-N-Me-Ala)4] including a partially ordered water centered in the cyclic peptide" [Hartgerink 1996]. Image used with permission.



"Atomic Force Microscopy image of the self-assembling peptide nanotube formed by the cyclic peptide cyclo-[(L-Glu-D-Ala)4] . The nanotube shown here has an unusual right handed super helical form" [Hartgerink 1996]. Image used with permission.

[Pum 1999] used crystalline bacterial cell surface layer (S-layer) proteins to assemble into two-dimensional arrays on silicon wafers and other surfaces. S-layer proteins, of which there are many, form surfaces on the outside of cells. [Pum 1999] used these proteins to position metals on a surface and then removed the protein by heating. Functional groups were repeated with the periodicity of the S-layer lattice (approximately 10nm) and this can be used to "... induce the formation of inorganic nanocrystal superlattices (e.g. CdS, Au, Ni, Pt, or Pd) with a broad range of particle sizes (5 to 15nm in diameter), interparticle spacings (up to 30nm) and lattice symmetries (oblique, square or hexagonal) as required for molecular electronics and non-linear optics" [Pum 1999]. S-layers can have oblique, square or hexagonal lattice symmetry with a unit cell of 3 to 30nm. S-layers are usually 5 to 10 nm thick with 2 to 8 nm pores.

While living things have shown us something of what nanotechnology might produce, most biomolecules are far too fragile for many aerospace environments. For example, it is unlikely that proteins or DNA can survive in rocket engines. One newly-discovered class of molecules, fullerenes, particularly carbon nanotubes [Iijima 1991], built from graphene sheets curved into a wide variety of close shapes, may lead to tougher, higher-temperature materials that can survive in a vacuum and other harsh environments. Fullerenes also have certain advantages for electronic applications.

Fullerene Nanotechnology

Carbon nanotubes are a novel form of carbon with remarkable electrical and mechanical properties [Dresselhaus 1995][Globus 1998b]. Carbon nanotubes can be visualized as rolled up graphite layers formed into cylinders. They may be single-or multi-walled. The tubes the may be rolled up with different windings (called chiralities) of the hexagonal sheet. Depending on the winding, small-diameter tubes have been shown to exhibit metallic or

semiconducting electronic properties. From [Globus 1998b]:

> We see that there is some evidence that fullerene based machines and, conceivably, machine phase materials based on them may be possible. Combined with the apparently remarkable mechanical and electrical properties of carbon nanotubes, there is some reason to believe that a focused effort to develop fullerene nanotechnology could yield materials with remarkable properties. Materials with electrical properties that could revolutionize circuit design and increased strength-of-materials leading to, among other things, opening the space frontier by radically lowering the cost of launch to orbit.

Note: machine phase materials are materials consisting of large numbers of machines plus supporting structures. Living tissue is a prime example.

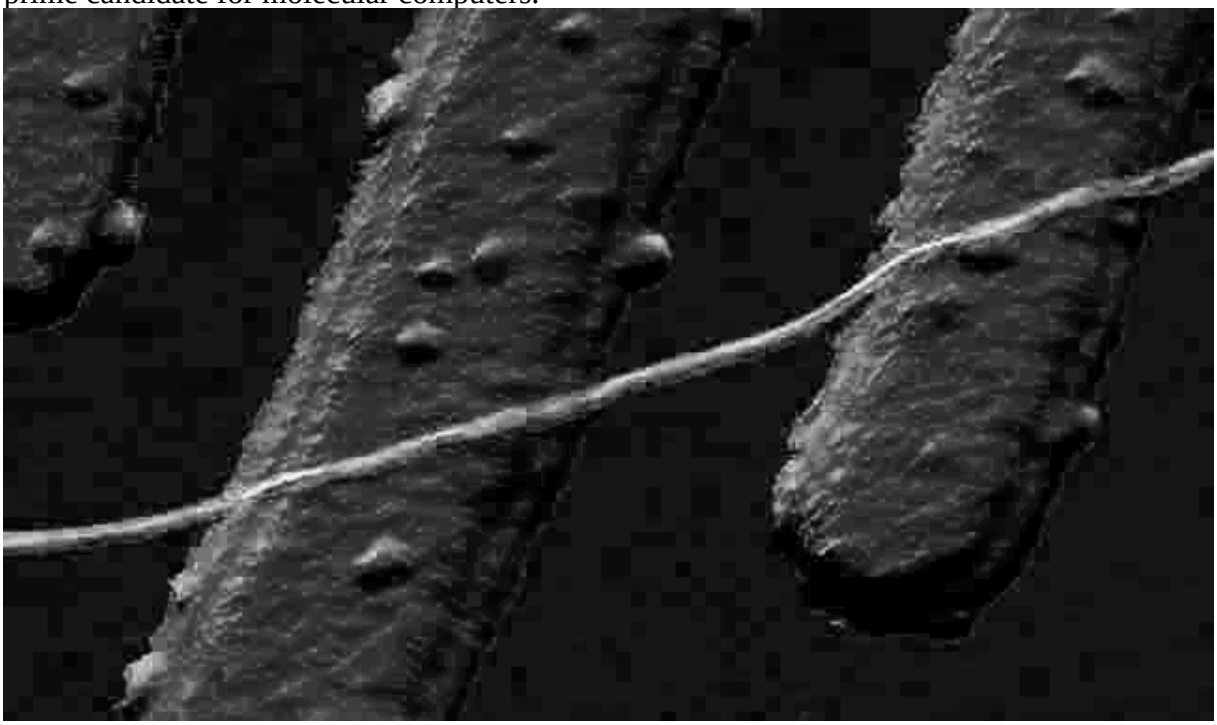
Since [Globus 1998b] was written, substantial progress has been made in manufacturing, controlling, and understanding carbon nanotubes and related structures. In particular, some of the predicted electronic properties of small-diameter single-walled carbon nanotubes have been confirmed, and a few devices have been built and tested. In addition, new numerical predictions have been made of ever more detailed devices and realistic systems. There has also been progress controlling the manufacturing process and in connecting carbon nanotubes to electronic components built by more conventional manufacturing techniques.

When a metallic and a semiconducting tube are joined, a device may be formed. For example, [Collins 1997] reports using an STM to explore the local electrical characteristics of single-wall carbon nanotubes. As the tip moved along the length of the nanotubes, well-defined positions were found where the current changed abruptly, in some cases exhibiting near-perfect rectification. These observations were consistent with localized, on-tube nanodevices predicted theoretically [Chico 1996].

[Service 1999] reported that Zettl, McEuen, and Fuhrer discovered an excellent diode formed from a pair of carbon nanotubes that crossed and didn't touch any neighbors. The properties of the diode were determined by attaching gold electrodes and passing current through the device. Unfortunately, the same article reports that Zettl and Collins discovered that both individual metallic carbon nanotubes and bundles are extremely noisy electrical conductors. The cause of the noise is currently unknown, but may be due to the impurities in the sample examined. If this is true, then the chemistry influences carbon nanotube electronic properties, which may be beneficial if it can be controlled.

[Tans 1998] reported the construction and testing of a field-effect transistor (a three-terminal switching device) consisting of a single semiconducting single-walled carbon nanotube in contact with metal electrodes. [Tans 1998] applied a large number of carbon nanotubes to a surface with pre-fabricated platinum electrodes placed on a silicon surface with an intervening 300 nm silicon oxide layer. [Tans 1998] found and measured over 20 individual tubes that were found draped over platinum electrodes. Some of these tubes exhibited metallic behavior. Others acted as the semiconductor component of a field-effect transistor. In other words, when a bias was applied to the gate electrode, the carbon nanotube effectively changed from an insulator to a conductor. This device, unlike diodes, exhibits gain. Gain is necessary for fan-out, making up for losses, and is considered essential for

practical devices. The estimated maximum frequency of the transistor is about 10 THz, achievable in part by reducing the width of the silicon dioxide surface to about 5 nm. [Tans 1998] was able to use standard bulk material models to qualitatively describe the carbon nanotube based transistor. Unlike the molecules used in [Ellenbogen 1999], there is currently no general methodology for controlling the production of carbon nanotubes with the precision necessary to devise electronic circuits. Also, carbon nanotubes are somewhat larger than Tour wires. However, if the synthetic challenges can be overcome, the higher current densities allowed and the fact that gain has been demonstrated makes carbon nanotubes a prime candidate for molecular computers.



Single-walled carbon nanotube draped across platinum electrodes [Tans 1998]. Image used with permission. http://vortex.tn.tudelft.nl/~dekker/nanotubes.html.

[Martel 1998] produced field-effect transistors from single- and multi-walled carbon nanotubes at about the same time. The abstract to this paper is so perfectly written is difficult to improve upon:

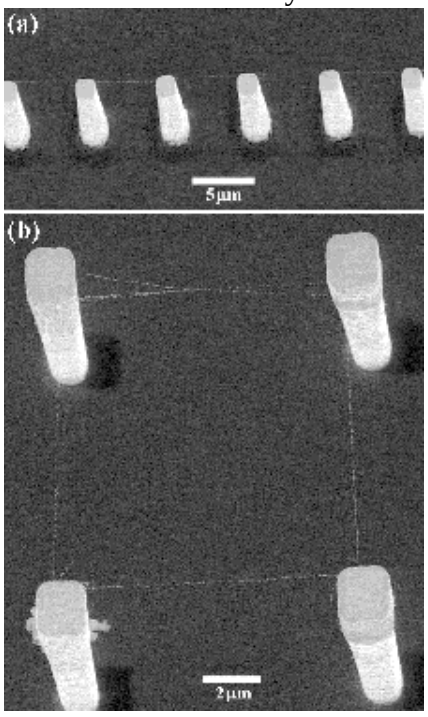
> "We fabricated field-effect transistors based on individual single-and multi-wall carbon nanotubes and analyzed their performance. Transport through the nanotubes is dominated by holes and, at room temperature, it appears to be diffuse and rather than ballistic. By varying the gate voltage, we successfully modulated conductance of a single-wall device by more than 5 orders of magnitude. Multiwall nanotubes showed typically no gate effect, but structural deformation -- in our case a collapsed tube -- can make them operate as field-effect transistors." [Martel 1998]

It is particularly remarkable that these transistors were fabricated by manipulating carbon nanotubes on a pattern surface until they were in the correct location for measurement. [Avouris 1999] reports on a number of interesting advances in fullerene technology produced by the same research group including the effect vander Waals forces of a substrate

on carbon nanotubes, which is substantial.

Constructing carbon nanotube computers is of no value if they cannot be connected to the outside world. [Zhang 1999] reported a relatively easy mechanism for connecting single walled carbon nanotubes to metals and silicon. [Zhang 1999] brought nanotubes into contact with silicon- and metal-based surfaces in a hard vacuum and heated the surface. The two materials became joined by carbide (a combination of carbon and the silicon or metal). Not only did [Zhang 1999] accomplish this with masses of carbon nanotubes on extended surfaces, they also connected titanium pads with carbon nanotubes. Current between titanium pads connected by carbon nanotubes varied linearly with voltage and resistance between them dropped dramatically after the heat treatment, indicating that a good electrical connection was created. [Zhang 1999] also used the technique to attach a bundle of single wall nanotubes to a titanium STM tip. Note that [Anantram 1999] predicted computationally that electron transport between carbon nanotubes and a substrate should be substantial, particularly if nanotube defects exist close to the cap.

For the most part, interesting carbon nanotube structures are found by producing large numbers of tubes in a relatively uncontrolled environment and examining the results molecule-by-molecule until an interesting structure is found. [Cassell 1999] reported a notable exception to this pattern. [Cassell 1999] built single-walled nanotube bridges suspended "... from catalyst material placed on top of regularly patterned silicon tower structures." Single-walled carbon nanotubes are grown from metal catalysts. The silicon towers, topped by catalyst metals, were constructed using conventional techniques, then carbon nanotubes were grown from the catalyst. Most of the tubes fell over the edge of the catalyst when they become long enough. Those that fell onto an adjacent tower remained suspended over the substrate between the two towers. By controlling the location of the towers, specific patterns of carbon nanotubes were synthesized. For example:



Carbon nanotube "power line" and a square from [Cassell 1999]. The large white objects are

catalyst-tipped towers. The thin lines are carbon nanotubes. Image used with permission.

Major Challenges and Opportunities

Molecular Computers

Molecular computers are an obvious extension of decades-long miniaturization trends in computing technology. Major progress has been made in the last few years, both computationally and experimentally, in understanding and manipulating organic molecules and carbon nanotubes with computational potential. The huge profits generated by the computer industry effectively guarantees large investments in molecular computer research and development. Aerospace will undoubtedly benefit greatly from these investments, but aside from long-term research conducted primarily by government laboratories and devices designed for high-radiation environments, the aerospace industry will probably not drive this technology, as most of the profits are derived from other sectors of the economy. Molecular computers will very likely be the first commercial fruits of the molecular nanotechnology revolution expected sometime in the 21st century.

Molecular Machines

In the short term, substantial progress in understanding biological molecular machines may be expected as the biotechnology revolution proceeds. The more difficult problem of using these machines in artificial devices can expect a large market for implantable medical devices. Unfortunately, most biomolecules cannot survive or function in many environments of aerospace interest because of high temperatures, extreme pressures, hard vacuum, high radiation, etc. Therefore, molecular machines based on other chemistry, perhaps fullerenes, must be developed. While there have been many successful experimental and computational studies of carbon nanotubes, deployment of operational fullerene-based molecular machines will require a great deal of research and development.

Macroscopic Products

The realization of enormous launch vehicle performance improvements suggested by theoretical nanotechnology studies [Drexler 1992b] [McKendree 1995] require atomically precise macroscopic products. To date, nearly all progress in molecular nanotechnology relates only to very small things, mostly molecules or partially ordered molecular aggregates. Integration into larger systems has not been accomplished. Two mechanisms have been proposed to build larger objects: self-assembly and replication. Self-assembly usually requires an aqueous environment incompatible with many aerospace applications. Furthermore, the resulting aggregates are usually held together with relatively weak hydrogen bonds, although sometimes these weak bonds are a precursor to stronger covalent bonding induced by light or some other factor. In any case, little progress in producing atomically precise macroscopic products has been made and producing such products remains a major challenge. There is one substantial current effort to produce macroscopic products using molecular nanotechnology, DARPA’s moltronics program. This program is attempting to develop molecular electronics, but required all proposals to directly address the system architecture (as [Collier 1999] does); not simply develop individual molecular

electronic components.

Replication

Biological systems have used reproduction to build macroscopic objects for over three billion years. However, artificial replication remains a largely theoretical field, although simple self-catalytic chemical systems have been developed [Lee 1996]. Current efforts in artificial replication are largely unfunded work by individual scientists. There's no obvious source of major research funding for this arena, although the long-term promise is enormous. In addition, there is substantial, well-founded concern that artificial microscopic replicators might get out of control and do serious harm. Thus, development of artificial replication faces not only major technical and developmental hurdles, but substantial safety concerns that must be thoroughly addressed in practice as well as in theory.

Conclusions

Molecular nanotechnology has enormous potential to improve aerospace systems. Substantial progress has been made in the last few years, particularly in the manipulation and visualization of matter at the atomic scale. Increased attention and funding brought by success will almost certainly accelerate progress in the future. Molecular nanotechnology, once scorned as "science-fiction" or "a mere dream," is now comfortably mainstream, as evidenced by frequent references to nanotechnology in *Science*, *Nature*, and other scientific journals and by the fact that the last three Foresight Conferences on Molecular Nanotechnology have had recent Nobel laureates as their keynote speakers. Progress, in fact, has been much quicker in some ways than many practitioners expected. Nonetheless, the closing comments of [Globus 1998a] are still true today:

> Nanotechnology advocates and detractors are often preoccupied with the question "When?" There are three interrelated answers to this question ...:
>
> 1. Nobody knows. There are far too many variables and unknowns. Beware of those who have excessive confidence in any date.
> 2. The time-to-nanotechnology will be measured in decades, not years. While a few applications will become feasible in the next few years, programmable assembler/replicators ... will be extremely difficult to develop.
> 3. The time-to-nanotechnology is very sensitive to the level of effort expended. Resources allocated to developing nanotechnology are likely to be richly rewarded, particularly in the long term.

Acknowledgements

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Note: many of the links are to sites that require a subscription.

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