

MODELING NANOSCALE CARBON STRUCTURES

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Abstract

Physical models are indispensable tools for understanding and teaching three-dimensional molecular geometries. This research is directed at presenting the relationship between the structure of materials on a nanoscale and their resultant properties and possible applications. The feasibility of novel modeling systems that not only serve as a visual representation of nanostructures, but also present an analogy for the bonding behaviors of atoms was explored in this research. New mechanisms for joining atoms were developed in order to simulate different types of bonding. All bonding mechanisms are internal to the atom module, eliminating the need for any external representation of bonds. Ionic and polar bonding are represented by embedded magnets; covalent and metallic bonding are achieved using a system of self-reorienting magnets. These mechanisms were then incorporated in the design of the Carbon Allotrope Modeling Modules (CAMMs), a modular molecular modeling kit capable of representing a number of carbon allotropes including graphite, diamond, buckminsterfullerene and nanotubes. Functional models were rapid prototyped, which allows multiple design, testing, and assessment iterations in a time- and cost-efficient manner. Students can build molecules and crystal lattices intuitively and in an atom-by-atom manner, allowing them to discover the geometry of nanostructures and their resultant material properties.

Keywords: carbon nanostructure, buckminsterfullerene, nanotube, rapid prototyping, physical

1. Introduction

Carbon allotropes have, for a long time, been used for both low- and high-technology applications. In industry, diamond is used extensively in cutting tools and abrasives. At the other end of the technology spectrum, diamond is fabricated into lenses for use with lasers. Another allotrope of carbon, graphite, is best known for its use in pencils. Its applications, however, extend far into industry. Graphite is used as dry lubricant for machinery and also as a conductive coating for electronic devices. These materials represent only two allotropic forms of carbon, a class of materials that has been ever-expanding since the mid-80's.

In 1985, in a laboratory at Rice University, Richard Smalley, Bob Curl, and Harold Kroto created and observed a new class of allotropic carbon, the fullerene [1]. Named after Buckminster Fuller, the inventor of the geodesic dome, the term "fullerene" encompasses a number of structures composed of even-numbered groupings of at least 32 carbon atoms arranged in a spherical geometry. C₆₀, often referred to as a buckminsterfullerene or buckyball, is the most common and notable of these allotropes.

In the early 90's, a new member of the carbon family was observed, the nanotube. On a nano-scale, the structure of this allotrope can be described as a cylinder formed by “rolling” a sheet of graphite into a tube. Nanotubes exist either as open-ended structures, like straws, or capped with a partial buckyball at each end, a geometry resembling a sausage link or gelatin capsule.

Engineers are exploring the potential applications of buckyballs and nanotubes in the fields of medicine, computers, and structural materials. It is important for engineers and students alike to be able to visualize and interact with the geometries of these new materials in order to achieve a better understanding of their physical properties. This research is directed at presenting the relationship between the structure of materials on a nanoscale and their resultant properties and possible applications. Physical models have been used to illustrate the hardness of diamond or the slipperiness of graphite. Similar models could also illuminate properties of buckminsterfullerenes and nanotubes, providing more insight into the development of new applications for these materials.

1.1 background on bond geometry

The carbon allotropes considered in this project were diamond, graphite, buckminsterfullerene and nanotube. Diamond (Figure 1a) exhibits an sp^3 hybridized orbital, atoms bond at angles of 109.5° causing a tetrahedral lattice structure [2].

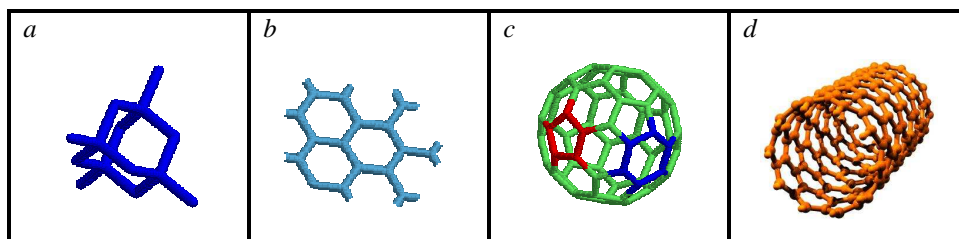
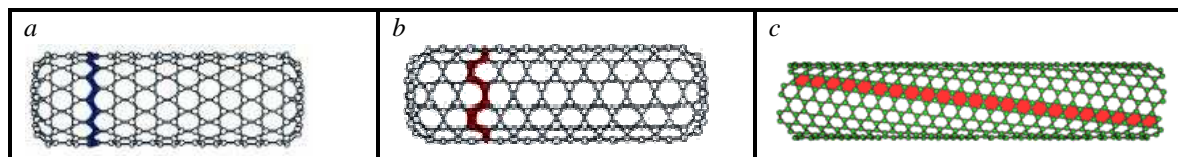


Figure 1 Geometries of a) diamond, b) graphite, c) buckminsterfullerene, and d) nanotube

Graphite, buckminsterfullerenes and nanotubes (Figures 1b, 1c, and 1d respectively) all exhibit sp^2 hybridized orbitals; each atom in these structures bonds to three neighboring atoms. Graphite exists as a trigonal planar structure, forming sheets of hexagonally bonded atoms. Each atom in the buckminsterfullerene bonds to three neighboring atoms such that two bond angles of 120° and one of 108° are formed. The 120° bonds produce hexagons (highlighted in blue) while the 108° bonds form pentagons (red). The resultant arrangement of carbon atoms defines the vertices of a truncated icosahedron.

Nanotubes can be visualized as rolled sheets of graphite. Depending on the orientation of the bonds with respect to a circumferential ring, nanotubes can be classified into three types: zig-zag (Figure 2a), armchair (Figure 2b), and chiral (Figure 2c). The bond angles of a nanotube are nearly 120° , but deviate to varying extents determined by the tube's diameter, bends along its length, and its type (zig-zag, armchair, or chiral).



<http://www.ncnr.nist.gov/staff/taner/nanotube/types.html>

Figure 2 Orientation of bonds in a) zig-zag, b) armchair, and c) chiral nanotubes [3].

1.2 objective

The purpose of this research was to develop a modular physical model with which students could assemble the different allotropes of carbon. The model kit was developed to meet specific criteria. The Carbon Allotrope Modeling Modules (CAMMs) were designed so that each carbon allotrope can be constructed from a single repeating CAMM (a sphere representing the carbon atom); all mechanisms for bonding are internal to these atoms.

By eliminating the need for additional connector pieces to form bonds, this model also avoids the suggestion that bonds are separate entities that are added to atoms. Attaching to each other by a system of self-reorienting magnets, atoms are designed to bond in geometric orientations that are present in the actual materials. Using CAMMs, students can build molecules and crystal lattices intuitively and in an atom-by-atom manner. This assembly process allows them to discover the geometry of nanostructures and the resultant material properties, thus facilitating tactile/kinesthetic learning.

The scope of this endeavor is limited to the representation of a number of carbon allotropes including graphite, diamond, buckminsterfullerene and nanotubes. Other model kits are being developed to represent nanostructures of other materials.

1.3 existing modeling kits

While determining the goals for the CAMM Kit, other molecular modeling products were examined. Although none of these individual kits fulfilled all the criteria for the CAMM Kit, each one featured at least one desirable characteristic.

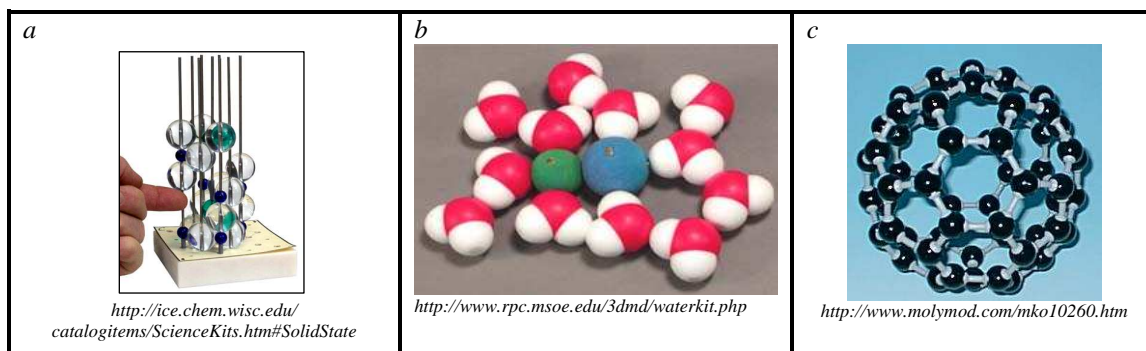


Figure 3 Existing molecular modeling products a) Solid State Model Kit [4], b) Water Kit™ [5], and c) MolyMod™ molecular models (assembled as a buckminsterfullerene) [6]

1.3.1 Solid State Model Kit (SSMK)

The Solid State Model Kit (Figure 3a), developed by the Institute for Chemical Education at the University of Wisconsin-Madison[7], uses a system of rods, beads and spacers to represent extensive crystal structures. This modeling kit is capable of representing a truly expansive array of crystal structures. Additionally, the SSMK model is capable of illustrating some structural properties including slip planes as shown above.

A student using the SSMK in essence builds structures by following a recipe. An in-depth guide outlines the assembly of dozens of structures, detailing explicitly the selection of a base and appropriate template (the kit comes with two bases and more than twenty templates), the placement of rods in the base, and the placement and size of beads and spacers. Beads and spacers of varying sizes are then threaded onto rods in sequenced layers, thus building a crystal structure by stacking beads upwards. Using the SSMK is not an intuitive process. It does not allow for the discovery of structures; this process of discovery was an important criteria for CAMMs. Furthermore, the atoms do not “bond”; rather, the network of rods and spacers imposes their proximity.

1.3.2 Water Kit™

The Water Kit™, developed by the Center for BioMolecular Modeling at the Milwaukee School of Engineering, represents phenomena associated with water such as freezing or the dissolving of NaCl (Figure 3b). Though the Water Kit™ only addresses a limited range of molecular structures and behaviors, the kit incorporates a novel feature: the mechanism for bonding is internal to each molecule or ion. Magnets, contained within the water molecules and imbedded on the surface of the Na⁺ and Cl⁻ ions, eliminate the need for any extra parts to represent

bonds. The representation of atoms bonding because of some intrinsic properties — rather than a bond being a separate entity imposed on or attached to two atoms — is a desirable feature.

1.3.3 *MolymodTM molecular models*

The MolymodTM molecular models, distributed by Spiring Enterprises Ltd. [8], are possibly the most versatile kits. The kits are comprised of two basic elements, small socketed spheres (representing atoms) and peg-ended connectors (representing bonds). The number and placement of sockets on each sphere is dictated by hybridized orbital theory. The combination of connectors and atomic spheres allows nearly any molecular combination ranging from crystalline structures to fullerenes to organic chain molecules. The MolymodTM product places a lot of emphasis on the representation of bonds. The kit also includes more flexible connectors that can be bent in order to represent the pi bonds present in double or triple bonds.

The most notable accomplishment of the MolymodTM is the adaptability of the individual modules. Each sphere merely represents an atom of a given size and hybridized orbital. Thus, the same atom module representing sp^2 carbon is used to model graphite, buckminsterfullerenes and nanotubes, despite the differences in bond angles. This adaptability is a result of the flexible nature of the plastic connectors. Though the sockets on the sp^2 sphere are spaced 120° apart, the connectors can deform slightly to create different angles. It is this external representation of bonds, however, which will be eliminated in the design of the CAMM Kit.

2. Design Process

2.1 solid freeform fabrication

Solid freeform fabrication (SFF) refers to a number of technologies that employ additive manufacturing methods to create physical objects from computer-generated models. A common application of SFF is rapid prototyping (RP), creating models or functional prototypes without the fabrication of expensive tooling (*e.g.* metal molds, dies, etc.). Using RP, multiple designs can be produced and tested in a short period of time; successful designs can then be improved and recreated in successive design iterations. The development of the Carbon Allotrope Modeling Modules relied on the Z Corporation's Z406 3D Printing system to facilitate such an iterative design process.

The rapid prototyping process begins with the generation of a computer model. Designs for this project were created using SolidWorks®. The SolidWorks® model is converted to an .STL (STereoLithography) file, which stores data about the surface of the model as a polygonal mesh.

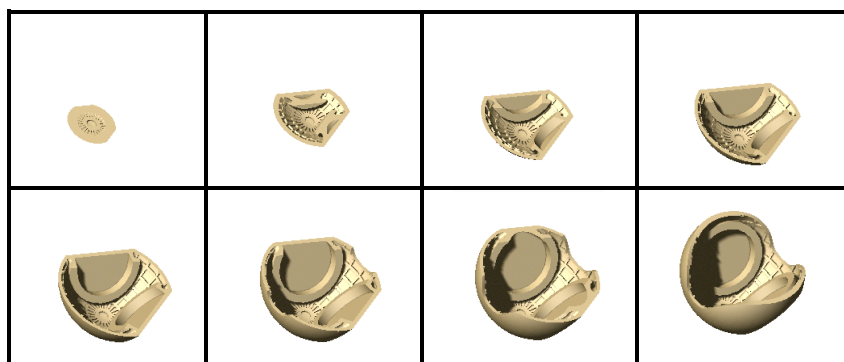


Figure 4 SolidWorksTM depiction of the stages of an SFF-built model.

The Z406 3D printer uses a plaster-based powder as the building material. Print heads deposit colored ink and liquid binder onto a thin layer of this plaster to create a cross-sectional slice as defined by the .STL data. The build platform is then lowered 0.004-0.006 inch and a thin layer of fresh plaster is distributed evenly over the build surface. Another cross-section is printed on top of and subsequently fused to the previous cross-section. The model

is again lowered and the process is repeated, creating and fusing new strata. And so, a physical model is constructed in a vertical, layer-by-layer manner (Figure 4).

The time and cost benefits of the Z406 were essential in the design and testing of successive iterations. Even minimal testing required multiple modules to be produced. Since the components of the module were relatively small (about one inch in height), a build could be completed in less than two hours. The quick build time allowed a model to be built, infiltrated, assembled, tested, redesigned and rebuilt within the span of a week. The color capability of the Z406 was an additional benefit.

2.3 modes of simulating atomic connections

The mechanism by which the atomic modules attach to one another was an area of thoroughly investigated over the course of the research. Though mechanical methods of connection were considered, magnetic attraction was the prominent mode explored. The models contain disc-shaped NdFeB rare earth magnets.

2.3.1 hetero bonding

Hetero bonding mechanisms utilize two different components (often referred to as the male and female) which are designed to connect specifically with the feature of the opposite kind. Most mechanical modes of connection fall into this category. Velcro™, for example, is a hetero connection; loops of fine thread mate with small plastic barbs. The Molymod™ model also makes use of hetero bonding, mating the peg at the end of a “bond” with a socket in the “atom”.

The Water Kit™ produced by the Center for Biomolecular Modeling employs fixed magnets, another hetero connection (one end of a magnet will only attract the opposite pole of another magnet). The water molecules as well as the models for the sodium and chlorine ions contain magnets with fixed orientation. By correlating the polarity of the magnets with the electronegativity of the atoms, this model limits the possible interactions among and between the water molecules and ions. While the polarity of fixed magnets provides a useful analogy for the intermolecular forces exhibited in ionic bonding, hydrogen bonding and dipole-dipole attraction. The same mechanism cannot be extended to represent the covalent bonds exhibited in allotropes of carbon.

2.3.2 bi bonding

There are three main possible instantiations of a bi bonding mechanism: a dual-sexed system in which one component will mate with either the opposite kind or with itself; a three-sexed system in which a third component is added to an existing hetero system such that it may mate with either of the previous components; or a combination in which a third sex may bond to either existing component or itself. The third mating scheme is of particular interest in modeling atomic bonding. Such a mechanism has potential to represent ionic, metallic and covalent bonding.

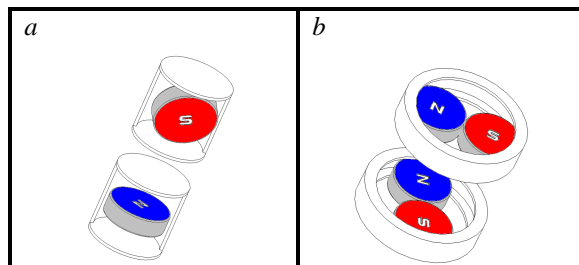


Figure 5 Example of a) flipping magnets and b) spinning magnets

Preliminary designs attempted to achieve a bi bonding scheme by allowing magnets to flip. Rather than affixing a magnet to the surface of the atom, the magnet was contained in a cylinder within the module (Figure 5a). Provided that the length of the cylinder was marginally greater than the diameter of the magnetic disc, the magnet could flip.

In this way, if a magnet were to encounter another of the same polarity, it would simply reorient itself to form a bond.

In practice, the flipping magnet scheme did not work satisfactorily. The cylinders that accommodated the flipping magnets extended from the inner surface of the sphere shell inwards radially. The cylindrical openings were blocked by means of a marble positioned at the center of the sphere. The magnetic attraction within the sphere, however, caused the magnets to position themselves at the bottom of the cylinder. To overcome this attraction and form a bond, the spacing between magnets in two different atoms would have to be less than that between magnets occupying the same sphere. To create sufficient internal spacing for a module with a tetrahedral orientation of magnets (required for modeling the diamond lattice), the atom would have to be roughly the size of a racquetball. As a result, a single module, let alone an extensive crystal structure assembled with such modules, would be certainly large and unwieldy.

2.3.3 *homo bonding*

A homo bonding scheme requires only one component which is capable of bonding to itself. Such a bonding scheme is analogous to covalent or metallic bonding. A homo bonding mechanism was utilized in the final design of the CAMM Kit to simulate the covalent bonding between identical atoms (Figure 5b). Each bonding site contains a pair of magnets connected side by side such that both polarities are represented. These magnets were again confined within a cylinder (the exposed end of the cylinder is covered with a small disc), but the height of the cylinder is insufficient for flipping. And so, the magnets are only free to spin within the cavity. When a magnet pair encounters another, they rotate about their centers to align opposing polarities. Since the cylindrical containers are shallow, the magnet pair cannot move towards the center of the sphere. Rather, it stays close to the surface of the sphere, a position conducive for strong and stable bonding.

3 Results and Conclusions

3.1 analysis of Carbon Allotrope Modeling Modules

The CAMM Kit (Figure 6) includes four different kinds of components: three different spherical modules to assemble diamond, graphite, and buckminsterfullerenes and ring-shaped, multi-atom modules which stack to form armchair nanotubes. To expand the functionality of the CAMM Kit, additional modules representing hydrogen and OH groups were created to allow for the representation of simple organic molecules. The OH module includes fixed magnets so that it could interact appropriately with the Water Kit™ produced by the Center for Biomolecular Modeling.

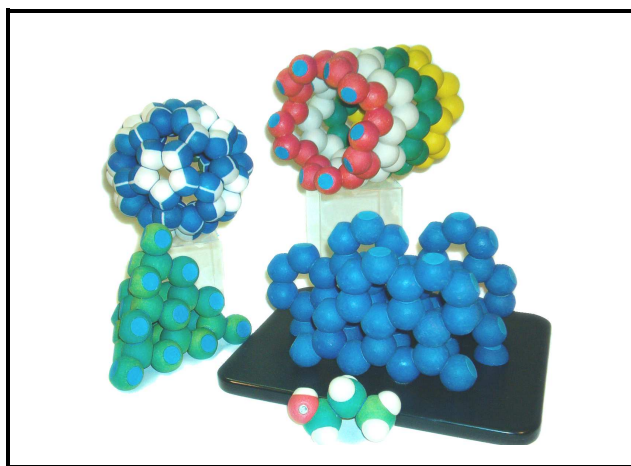


Figure 6 CAMM Kit modeling (clockwise from top left) buckyball, nanotube, graphite, propanol, diamond.

The final design of the CAMM Kit uses spinning magnets as the mechanism for bonding (Figure 7a). The surfaces of the exterior shell are flattened at points of contact to promote a stronger attraction between magnet pairs (Figure 7b) and to ensure bonding at the appropriate bond angles. Another benefit of this truncated-sphere shape is that assembled modules form space-filled representations of molecules.

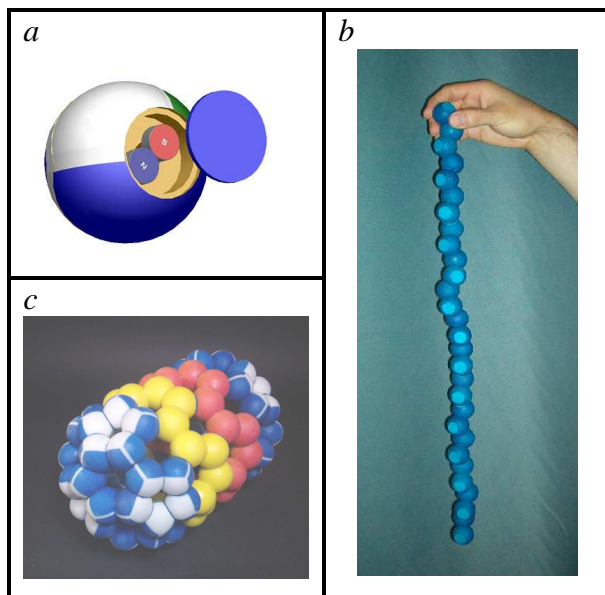


Figure 7 a) the inner-workings of a CAMM, b) demonstration of bonding strength, and c) C100 molecule

3.1.1 interactivity of CAMMs

CAMMs are designed to interact with modules of different types, and in fact, these interactions can yield a number of important molecules. For example, the nanotube-ring modules are of a type (armchair) and diameter (10 hexagons around) to cleanly transition to the buckyball structure. Combining the two kinds of modules allows for the representation of larger fullerenes and capped nanotubes. C100 (Figure 7c), an elongated fullerene, can be created using 60 buckyball modules and two nanotube rings (representing 20 atoms each).

CAMMs of different types can also be combined to form a variety of simple organic molecules. Hydrogen caps can be added to hexagons assembled using graphite modules forming benzene. Diamond modules can be similarly supplemented with hydrogen or OH groups to make chain or cyclical organic molecules. These molecules can then be attached to existing chains or benzene rings as functional groups.

3.1.2 additional features

The basic CAMMs are supplemented with additional features to highlight some salient characteristics of the structures being represented. The buckyball CAMMs are colored, so that when assembled, the surface of the buckyball is segmented into hexagons and pentagons. This coloring scheme highlights the hexagonal structure which is inherent in sp^2 structures. Furthermore, the surface pattern also serves as a guide for assembly; aligning lines or blocks of colors to form hexagons and pentagons results in a correctly assembled buckyball.

To illustrate the layered sheets formed by graphite, the graphite modules can be displayed on an accompanying base (Figure 6). The base features three rows of magnetic contact points – separated to scale with the distance of a C-C bond – to represent the distance between layers referred to as the van der Waals gap [9]. Furthermore, the middle row is elevated by a half-atom's height to produce the correct relative orientation of atoms in consecutive layers. Graphite modules can be assembled on this base, forming vertical sheets.

3.2 recommendations for the future of CAMMs

Graphite, nanotubes, and fullerenes all share sp^2 bonding structures; each atom bonds to three neighbors at angles ranging from 108-120°. Future CAMM designs may incorporate a mechanism for varying bond angles. Contact points would be flexible, allowing a small range of bond angles to be achieved. This would allow a single module to model a number of different allotropes including graphite and a wide range of fullerenes and nanotubes.

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