Exploring the Nanoworld with LEGO® Bricks

Featuring contributions from:

Dean Campbell
Ellen Freidinger
Moira Querns
Stacy Swanson
Arthur Ellis
Thomas Kuech
Amy Payne
Benjamin Socie
S. Michael Condren
George Lisensky
Robert Rasmussen
Todd Hollis
Richard Villarreal
Kristine Campbell

Copyright 2012

Board of Trustees of Bradley University, http://www.bradley.edu/
All rights reserved.

This project was supported, in part, by the
National Science Foundation,
http://www.nsf.gov/
through the University of Wisconsin-Madison Materials Research Science and Engineering Center on Nanostructured Materials and Interfaces,
http://mrsec.wisc.edu/

and by LEGO® Dacta®. LEGO, DACTA, RCX, and NXT are trademarks of the LEGO group and are used with special permission.
© The LEGO Group,
http://www.lego.com/
. The illustrations in these experiments are used here with special permission.

Any opinions, findings, or conclusions are those of the authors and do not necessarily reflect the views of the supporting agencies.

Contents

Foreword iv

Introduction v

Chapter One - Structures at the Nanoscale 1-1

1.1 What is a Solid? 1-1

1.2 Unit Cells 1-1

1.3 Solid Solutions 1-6

1.4 Liquid Crystals 1-7

1.5 Organic Structures 1-9

Chapter Two - Probing the Structure of Materials at the Nanoscale 2-1

2.1 Scanning Probe Microscopy 2-1

2.2 Charge-Coupled Devices 2-3

2.3 Photometry 2-6

2.4 Nuclear Magnetic Resonance 2-9

2.5 Chromatography 2-11

2.6 Diffraction and Wave Addition 2-11

2.7 Scanning Electron Microscopy 2-16

Chapter Three - Structure-Property Relationships at the Nanoscale 3-1

3.1 Polymer Cross-linking 3-1

3.2 Poisson's Ratios 3-3

3.3 Silicates 3-4

3.4 Metal Deformation 3-6

3.5 Composites 3-7

3.6 Giant Magnetoresistance 3-8

3.7 Plasmon Resonance 3-9

Chapter Four – Structures and Their Construction at the Nanoscale 4-1

4.1 Photolithography 4-1

4.2 Self-Assembly 4-2

4.3 Linear Nanostructures 4-3

4.4 Chain Reactions 4-4

4.5 Ferrofluid: Nanoscale Particles and Surfactants 4-5

4.6 Photonic Crystals 4-6

4.7 Dialysis 4-9

References / Additional Reading Ref-1

Book Assessment Form

Appendices – Building Instructions

Section 2.1 Appendix – Scanning Probe Microscopes

Section 2.2 Appendix – Charge-Coupled Device

Section 2.3 Appendix – Photometer

Section 3.2 Appendix – Poisson's Lattice

Section 3.6 Appendix – Giant Magnetoresistance Structure

Foreword

Science and technology at the nanoscale, the scale of individual atoms, are revolutionizing our ability to manipulate matter. Using our current experimental tools, we can image individual atoms and position them to create nanoscale architecture with customized functionality. Experts in many fields are predicting that we may be able to produce materials more cheaply and with less damage to the environment, create faster and more powerful computers, and provide more effective health care through genetic therapy and drug design. In short, nanoscience and nanotechnology have the potential to reshape our society. An excellent summary of developments in this field may be found at http://www.nano.gov/.

With generous support from the National Science Foundation (NSF), the University of Wisconsin-Madison Materials Research Science and Engineering Center (MRSEC) for Nanostructured Materials and Interfaces has launched an effort to make the nanoworld accessible and comprehensible to everyone. This booklet is an important part of our effort. Dean Campbell recognized that LEGO® bricks provide a safe, inexpensive, and widely available means for modeling the materials and tools that are part of nanoscale science and technology. Under Dean's leadership and with support from the NSF MRSEC, a set of LEGO-based models has been created for informing readers about structures at the nanoscale, tools for probing these structures, and relationships between structures and their properties. In addition to the NSF, we are also grateful to Robert Rasmussen of LEGO® Dacta® for his generous support of this project and to George Lisensky and Michael Condren for their assistance with editing this booklet.

This booklet and associated website (http://mrsec.wisc.edu/edetc/LEGO/index.html) are meant to be living products that will be updated as new technologies emerge that lend themselves to LEGO® modeling. We invite readers to send us their comments on the booklet and website as well as suggestions for extensions of this project.

Arthur B. Ellis, MRSEC Education/Outreach Coordinator

University of Wisconsin- Madison, Madison, Wisconsin

July, 2001

Introduction

The purpose of this booklet is to show how various physical and chemical principles related to nanoscale science and technology can be demonstrated with LEGO® models. Three-dimensional models are excellent tools for grasping structure-function relationships.

There are a number of reasons to consider using LEGO® bricks for this purpose. First, many people are familiar with LEGO® bricks, and most models can be built with a level of mechanical sophistication that does not intimidate or frustrate the user. Second, LEGO® bricks typically have many connection points, allowing tremendous flexibility in the structures that can be built. A set of bricks can be used to model structures of matter and the techniques used to study them.

This book is divided into four parts. The first part, *Structures at the Nanoscale*, presents basic concepts for describing solid structures. The second part, *Probing the Structure of Materials at the Nanoscale*, contains brief sketches of techniques used to determine the structures of solid materials. *Structure-Property Relationships at the Nanoscale*, the third part, links the atomic and molecular arrangement of matter to physical properties and introduces materials at the cutting edge of nanoscale science and technology, where the size of individual solid particles of material approaches molecular dimensions. The fourth part, *Building Structures at the Nanoscale,* describes methods and challenges of building nanoscale structures with macroscale equipment.

The authors are grateful to the National Science Foundation, through the University of Wisconsin-Madison Materials Research Science and Engineering Center (MRSEC) for Nanostructured Materials and Interfaces, Bradley University, and to LEGO® Dacta® for support of this project. We invite your comments on this book.

Dean J. Campbell, Associate Professor of Chemistry and Biochemistry

Bradley University, Peoria, Illinois

campbell@bradley.edu

NOTE: LEGO® brick dimensions will often be described by numbers of pegs on their top surfaces. For example, a 2x4 brick is 2 pegs wide and 4 pegs long.

Chapter One – Structures at the Nanoscale

LEGO® bricks (with their many colors and points of connection) are excellent tools for demonstrating the nanostructure or even the atomic-level structure of solids. For some of the activities below, you may also be interested in a solid state model kit produced by the Institute for Chemical Education (ICE), which uses spheres of different sizes in a Solid State Model Kit to create three-dimensional structures.

NOTE: LEGO® brick dimensions will often be described by numbers of pegs on their top surfaces. For example, a 2x4 brick is 2 pegs wide and 4 pegs long.

1.1 What is a Solid?

The three principal states of matter are gas, liquid, and solid (Figure 1.1). In gases, the particles, which are individual atoms or molecules, are far apart from each other and can move about freely. As a result, gases readily fit the shape of their container and can be easily compressed. In liquids, the particles are much closer together, so liquids are far more difficult to compress; the particles that make up liquids move about, enabling liquids to change shape easily. In solids, the forces between the particles are strong enough to hold the particles together in specific positions, causing solids to maintain their shape.

Figure 1.1 - Using 1x2 LEGO® bricks to model (left to right) gases, liquids, and solids.

1.2 Unit Cells

Many aspects of science deal with repeating patterns. Finding the repeating unit in a pattern enables scientists to simplify a large system. Many solids form crystals, in which particles arrange themselves in repeating patterns of atoms. The pattern repeats itself in all three directions (left and right; up and down; forward and backward) until the boundaries of the solid are reached. A two-dimensional analogy is wallpaper: from a representative part of the pattern, the entire wall surface can be tiled using the same pattern.

Consider a unit cell in the shape of a parallelogram. It produces a repeating pattern by being shifted in the direction of each of its sides by the length of that side.
For example, Figure 1.2 depicts an array of LEGO® bricks in a pattern. Four possible unit cells are outlined. Which ones are valid unit cells for this pattern?

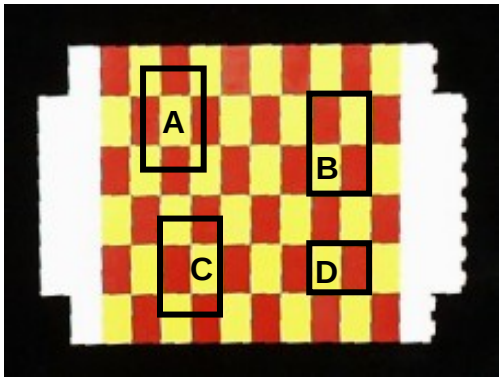


Figure 1.2 - Trial unit cells. A, B, C, and D are parallelograms. Which of these can be shifted along each of its edges by the length of the edge to create a replica of its contents?

If you picked A, B, and C, you are correct! In D, shifting (also called “translating”) the proposed unit cell up or down by the length of its sides does not generate the same pattern within the parallelogram. Figure 1.3 shows the pattern formed by replicating D.

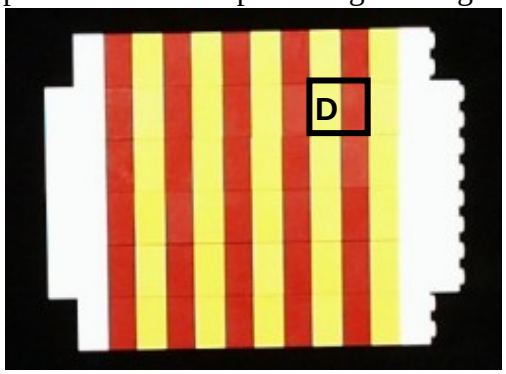


Figure 1.3 - The pattern formed by replicating D (black rectangle). Since D is not a unit cell of Figure 1.2, the generated pattern does not match Figure 1.2.

It does not matter whether the unit cell contains whole bricks (B), or only pieces of bricks (A), or both (C), as long as the pattern may be extended by repeated shifting of the unit cell to completely cover (tile) the surface with no gaps.

LEGO® bricks may be used to generate more challenging repeating patterns. Figure 1.4 shows another two-color repeating "brick wall" of LEGO® bricks. A unit cell can be outlined with overhead projector markers, as shown in the figure, and erased again with a wet paper towel.

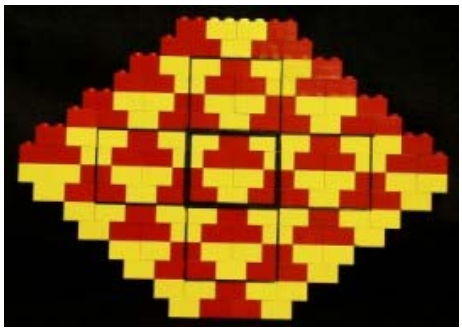


Figure 1.4 - Two-color 1x2 brick wall formed. A unit cell is outlined in black in the center and has been shifted in all four directions to show that all of the shifts yield parallelograms with identical contents to the original parallelogram.

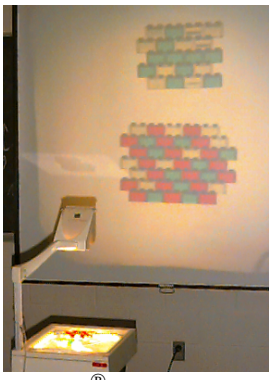


Figure 1.5 - With translucent LEGO® bricks, the brick walls can be shown to large groups using an overhead projector.

LEGO® bricks can also make 3-dimensional patterns that have unit cells. In Figure 1.6, left, the model resembles a 3-dimensional checkerboard. This pattern is similar to that adopted by table salt, sodium chloride, which is comprised of electrically-charged atoms called ions. In the right-hand part of Figure 1.6 sodium ions are represented by the smaller blue spheres and chloride ions are represented by the white larger spheres.

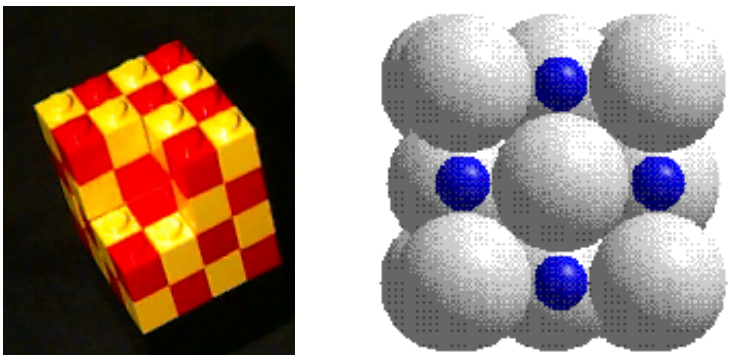


Figure 1.6 - (left) The sodium chloride structure as depicted with 1x1 LEGO® bricks. (right) The sodium chloride structure shown with small blue spheres representing sodium ions and the large white spheres representing chloride ions.

The sodium chloride unit cell is a cube whose corners lie at the centers of the eight corner spheres. Although the LEGO® structure has the correct alternation of atoms, it is less accurate than the structure on the right, because sodium and chloride ions have different sizes in the actual structure.

In many cases the atoms or ions (usually thought of as spheres) in a solid structure can be represented as various arrangements of bricks, shown in Figure 1.7. The arrangements are some of many possible LEGO® representations of atoms.

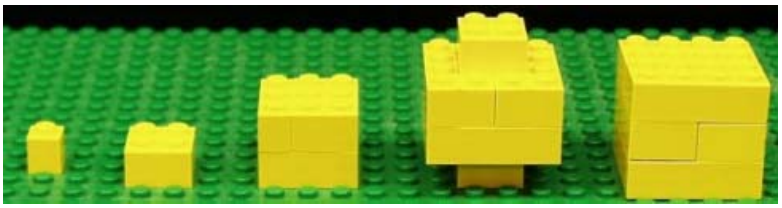


Figure 1.7 - Different possible arrangements of bricks to represent atoms (left to right): 1x1 brick; 2x2 brick; cluster of two 1x3 bricks and two 2x3 bricks; cluster of two 2x2 bricks and four 2x4 bricks; cluster of six 2x4 bricks.

These brick arrangements can be packed together similar to the packing of atoms in a real solid. The various arrangements of bricks to make atoms provide multiple ways of modeling a particular structure. Figure 1.8 shows various representations of the sodium chloride structure.

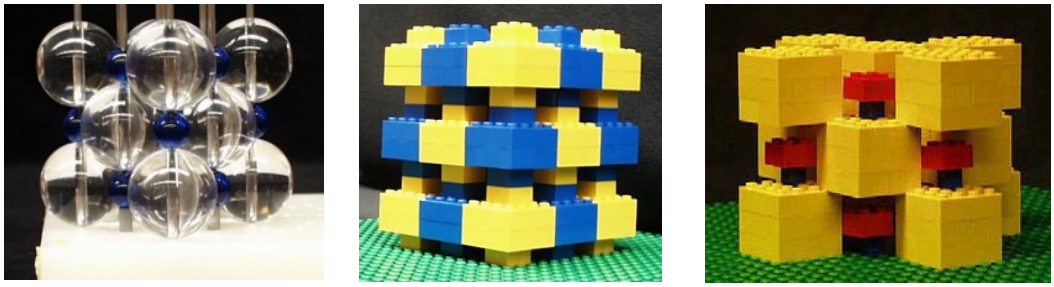


Figure 1.8 - Models of the sodium chloride structure, all featuring 13 sodium ions and 14 chloride ions. (left) Model made with the Institute for Chemical Education Solid State Model Kit - the small blue spheres represent the sodium ions and the large colorless spheres represent the chloride ions. (middle) LEGO® brick model made with clusters of two 2x2 bricks and four 2x4 bricks representing both sodium and chloride ions (right) LEGO® brick model made with clusters of six 2x4 bricks reperesenting chloride ions and red 2x2 bricks representing sodium ions (black 1x1 bricks have been added underneath each red brick as spacer supports).

Unit cells may be divided into layers of atoms. These layer sequences, as they are called, describe the positions of the atoms within the unit cell and can be used as instructions for building models of the unit cell. In each layer sequence, the bottom-most layer is repeated to form the top-most layer, which would serve as the bottom for another unit cell if the structure was extended by more layers upward. Figure 1.9 describes the layer sequence for a sodium chloride unit cell.

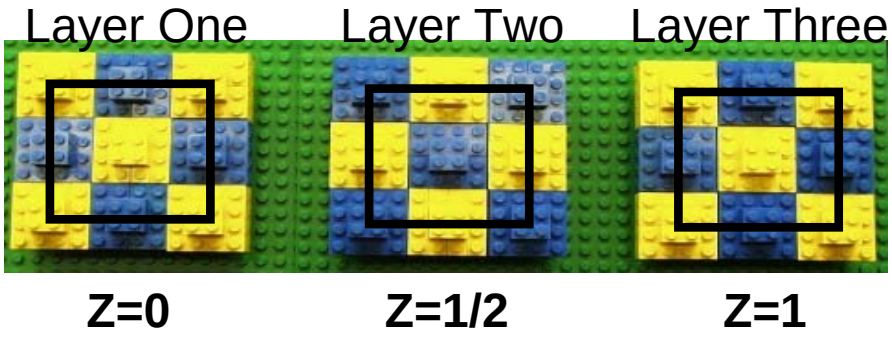


Figure 1.9 - The layer sequence of the sodium chloride unit cell depicted in Figure 1.8 (middle picture). Each cluster of two 2x2 bricks and four 2x4 bricks represents an ion. The black squares drawn over the pictures depict actual unit cell boundaries; the corners of the cubic unit cell lie at the centers of the 8 atoms at the cube's corners. Each layer is given a Z value indicating its “altitude” in the unit cell. The layer at the bottom of the unit cell is always given a value of Z=0. The layer at the top of the unit cell is always given a value of Z=1 and must be identical to the Z=0 layer. Intermediate layers are given fractional values such as Z=1/2.

LEGO® bricks can be used to model rather elaborate structures. Figure 1.10 shows models of the cube-shaped unit cell for diamond. Diamond, a form of carbon, is the hardest common material. Not only is it a precious gemstone, but it is commonly used as

an abrasive and cutting tool in industry. Its wear-resistance and superior ability to transport heat make it an important coating material, as well. The same structure is also possessed by silicon (the material that lies at the heart of computer integrated circuits), germanium, and one form of tin.

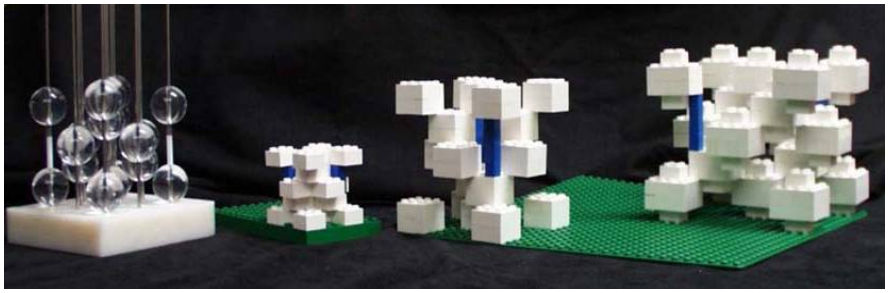


Figure 1.10 - Several models of the diamond unit cell, each comprised of 18 “atoms”. The model at the left is made with the Institute for Chemical Education Solid State Model Kit. The LEGO® brick models are made with: 2x2 bricks; clusters of two 1x3 bricks and two 2x3 bricks; and clusters of two 2x2 bricks and four 2x4 bricks (blue 1x1 bricks have been added as spacer supports).

One of the significant strengths of using LEGO® bricks to build atomic-level structures is the ability to build fractions of atoms for "bookkeeping" numbers of unit cell atoms. Many model kits can only depict entire atoms in a structure, but often only portions of atoms are contained within the boundaries of the unit cell. Figure 1.11 shows ways of representing fractions of atoms and Figure 1.12 shows a unit cell for sodium chloride using these fractional atoms.

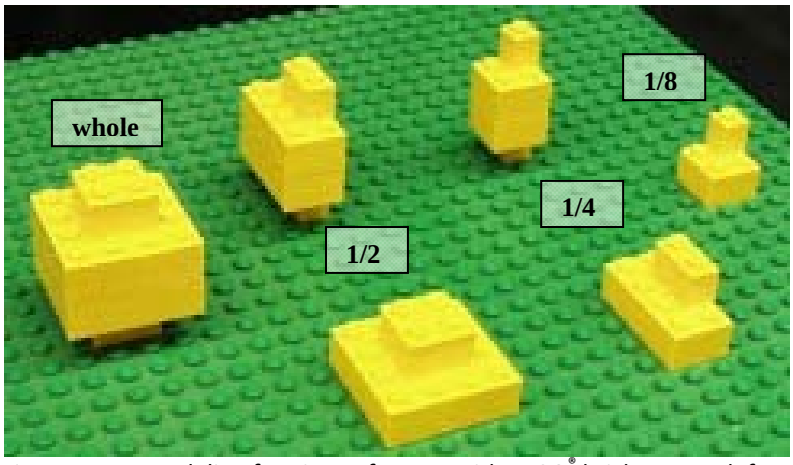


Figure 1.11 - Modeling fractions of atoms with LEGO® bricks. From left to right:
whole atom as a cluster of two 2x2 bricks and four 2x4 bricks,
1/2 atom as a cluster of two 1x2 bricks and two 2x4 bricks,
1/2 atom as a cluster of one 2x2 bricks and two 2x4 bricks,
1/4 atom as a cluster of two 1x1 bricks and two 2x2 bricks,
1/4 atom as a cluster of one 1x2 brick and one 2x4 brick,
1/8 atom as a cluster of one 1x1 brick and one 2x2 brick.

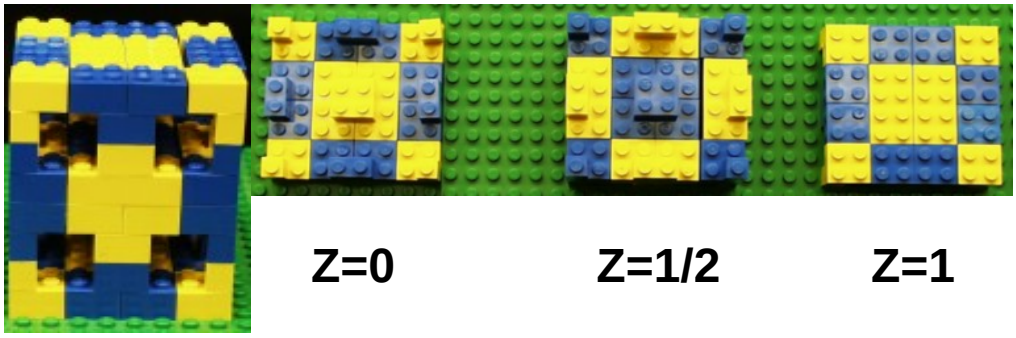


Figure 1.12 - The actual unit cell of the sodium chloride structure depicted in Figure 1.8 (middle) and Figure 1.9 built with fractional atoms, as well as the layer sequence for its construction, built from:

whole sodium ion as a cluster of two 2x2 bricks and four 2x4 bricks,
four 1/4 sodium ions as clusters of two 1x1 bricks and two 2x2 bricks,
eight 1/4 sodium ions as clusters of one 1x2 brick and one 2x4 brick,
four 1/2 chloride ions as clusters of two 1x2 bricks and two 2x4 bricks,
two 1/2 chloride ions as clusters of one 2x2 bricks and two 2x4 bricks,
eight 1/8 chloride ions as clusters of one 1x1 brick and one 2x2 brick.

Note that there are equal quantities of sodium and chloride ions (4 each) within the boundaries of the unit cell, which is consistent with the known formula for sodium chloride (NaCl).

The website associated with this book contains building instructions for a number of unit cell models. These can be accessed from the page called LEGO® Molecular-Scale Models, http://mrsec.wisc.edu/Edetc/LEGO/index.html. Building instructions for many atomic-scale element structures can be accessed from the page called LEGO® Periodic Table, http://mrsec.wisc.edu/Edetc/LEGO/LEGO%20PT%20final.html. Most instruction sets follow essentially the same format. At the top of each set of instructions is a picture of LEGO® units representing atoms or ions for that structure (remember other brick arrangements representing atoms are often possible). Following that is a series of pictures showing a layer-by-layer assembly sequence of the atoms and other support structures in the unit cell. The pictures show each individual layer of atoms starting from the bottom layer and building up. This is called the layer sequence for the unit cell. Squares drawn over the pictures depict unit cell boundaries. Intermediate layers are given fractional values such as Z=1/2, representing atoms with centers halfway up the unit cell. In addition to the layer sequence, there are pictures depicting the building-up of the unit cell as each layer is added.

1.3 Solid Solutions

When a solid, liquid, or gas is completely dispersed into atoms or molecules in a liquid, we refer to that liquid as a solution. An example of a solution would be salt water, which is composed of sodium chloride (which we commonly use as table salt) dissolved in water. In a similar fashion, one solid can sometimes be dispersed throughout another solid, creating a solid solution. Solid solutions can form crystals with unit cells. A simple model of a solid solution can be made with LEGO® bricks. Figure 1.13 (left) shows a typical LEGO® "brick wall" made with two colors of bricks of equal size. This wall was made by randomly flipping a coin, with “heads” arbitrarily directing us to add a red brick

and “tails” arbitrarily directing us to add a yellow brick. Therefore, the chance of any brick being yellow is 0.5 and the chance of any brick being red is 0.5.

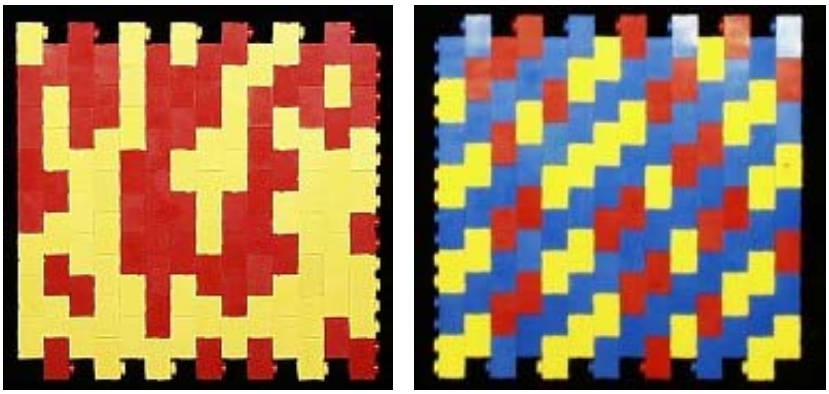


Figure 1.13 - Models of random solid solutions produced by 1x2 bricks.

Note that if we ignore the fact that the LEGO® bricks have different colors, the bricks are arranged in a repeating pattern that has a unit cell. If we define the yellow bricks as element A and the red bricks as element Z, we could give this solid solution a chemical formula, $A_{0.5} Z_{0.5}$. The decimal subscripts here indicate the relative numbers of A and Z atoms. Brass is an excellent example of a real solid solution. It is a binary (two-component) alloy of the metals copper and zinc. Often in real solid solutions the atoms are not identical in size.

LEGO® bricks can also model more complex solid solutions. Figure 1.13 (right) shows a "brick wall" pattern involving 3 colors. To make this wall, a blue brick was set in place, then either a yellow or red brick was added, then another blue brick, followed by either a yellow or red brick, and so on. The yellow and red bricks were chosen at random in a 1:1 ratio by flipping a coin. If we ignore the color distinction between the yellow and red bricks, we have a repeating pattern that has a unit cell. This time the structure can be written as $ZA_{0.5} Q_{0.5}$, where blue bricks are element Z, yellow bricks are element A, and red bricks are element Q.

Solid solutions are important not only for metal alloys, but also for semiconductors. For example, many light-emitting diodes (LEDs) use solid solutions containing gallium (Ga), phosphorus (P), and arsenic (As). Half of the atoms in these solid solutions are Ga, but the other half can be any ratio of P to As. By changing the ratio of P to As, the color emitted by the LED when it is excited by electrical energy can be tuned. The structure of GaP, GaAs, and $GaP_x As_{1-x}$ is referred to as the zinc blende structure, but it can also be thought of as similar to the diamond structure with more than one kind of atom involved.

1.4 Liquid Crystals

Most solids have an ordered structure, with molecules or atoms arranged into crystals. As the solid is heated, the molecules lose their order and become a liquid in a process called melting. Some solids, though, seem to melt twice, first to form a cloudy liquid, then a

clear one. The cloudy liquid displays a property called birefringence, in which a beam of light shone through the sample splits into two beams. This property comes from the ordered nature of crystals in most solids. The cloudy liquid, then, must have some order. It is therefore, a paradox: a liquid that is a crystal, or a liquid crystal.

When a crystal is made up of roughly spherical molecules it has only one melting transition. The relative position of the spheres can be ordered or not. But if a crystal is made up of molecules that are not spherical, then there are other possibilities. Some molecules are shaped like rods, and in a crystal they have order not only in their position, but also in their orientation. In a crystal, the rod-shaped molecules are all locked into a particular position and orientation. This is a highly ordered state. The rod-shaped molecules are ordered in both position and orientation. When heat is added, the molecules begin to agitate and they push away from each other. Positional order is lost. But they are still close enough together that they cannot lose their orientational order. Finally, as more heat is added, the molecules push farther away form each other and lose their orientational order. This random system is a true liquid.

Because liquid crystals have some crystalline structure, they also have some of the properties that solids have. This combination of refractive properties and liquid mobility makes liquid crystals extremely useful in display screens (LCDs), dyes, and other technologies.

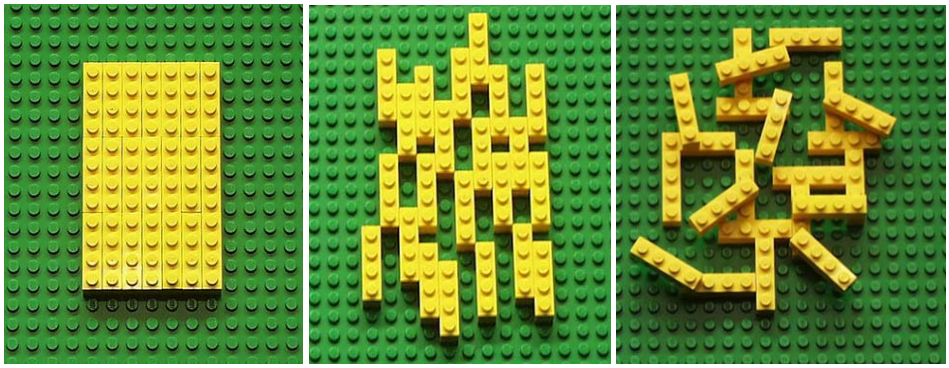


Figure 1.14 – (left to right) 1x4 LEGO® brick representations of a crystalline solid, one type of a liquid crystal phase, and a liquid.

Sometimes the molecule, in addition to being a shape other than spherical, is chiral. In this case, the molecules orient themselves at slightly skewed direction from the molecules below it and above it. The result is a spiral pattern, like a screw or a helix. When a beam of polarized light shines through a sample in this phase, the polarization of the light is twisted to emit parallel to the orientation of the top molecule.

Each vertical layer of molecules is oriented slightly askew from the one below it. A light shining through a polarizing filter enters at the bottom, travels through the spiral, and leaves through a perpendicular polarizing filter. The red bricks represent the polarization of the beam of light. If the molecule, in addition to being chiral, has a dipole, the orientation can be changed with the application of an electric field. Thus, the molecules can be aligned so that with the application of light through a filter, they transmit light

through a perpendicular filter at the top. With the application of an electrical field, their orientation is changed, the helix is lost, and no light is transmitted.

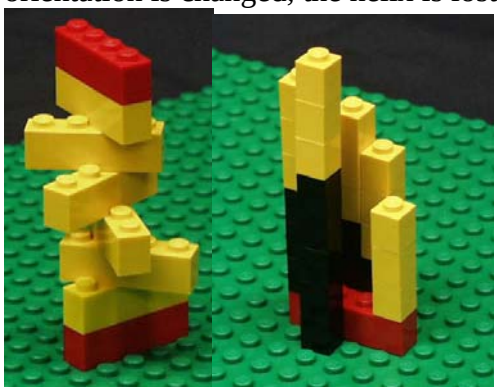


Figure 1.15 – (left) LEGO® bricks arranged to represent the cholesteric liquid crystal of a chiral molecule. (right) LEGO® bricks arranged to represent the charged molecules above under the influence of an electric field. Their orientation has been changed and light is no longer transmitted through the top filter. The red brick is the initial beam of light. The black 1x1 bricks are placeholders. In the two models above, the yellow 1x4 bricks and the three yellow 1x1 bricks represent the same molecule. The dimensions are the same, and using two kinds of models allows the molecules to be shown in both horizontally oriented and vertically oriented positions.

1.5 Organic Structures

Examination of the diamond structure shown in Figure 1.10 reveals that LEGO® bricks may be used to represent tetrahedral arrangements of atoms. Many carbon-containing compounds, referred to as organic compounds, contain carbon atoms chemically bonded to other atoms in a tetrahedral geometry. Chiral structures and polymers can also be represented with LEGO® bricks. The website associated with this book contains building instructions for a number of organic structure models. These can be accessed from the page called LEGO® Molecular-Scale Models, http://mrsec.wisc.edu/Edetc/LEGO/index.html.

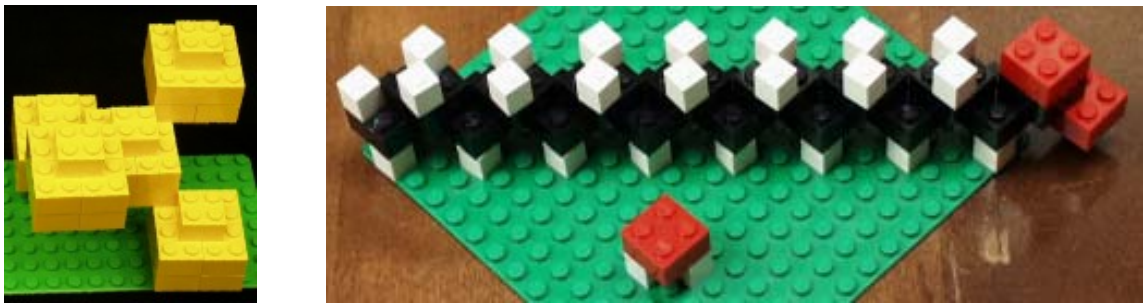


Figure 1.16 – (left) Representation of a tetrahedral arrangement of atoms with five clusters of two 2x2 bricks and four 2x4 bricks. (right) Representation of palmitic acid anion and a water molecule. Like the color coding of many organic chemistry models, the 16 black 2x2 bricks represent carbon atoms, the 33 white 1x1 bricks represent hydrogen atoms, and the 3 red 2x2 atoms represent oxygen atoms.

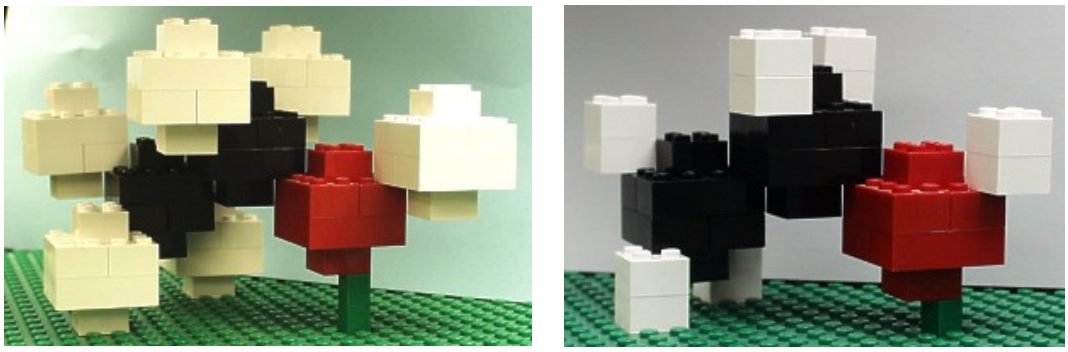


Figure 1.17 – Two representations of an ethanol (C_2H_6O) molecule. Like many organic chemistry models: black = carbon, white = hydrogen, red = oxygen. (left) All atoms are comprised of clusters of two 2x2 bricks and four 2x4 bricks. (right) The hydrogen atoms have been changed to smaller clusters of two 2x2 bricks (green 1x1 bricks have been added as spacer supports)

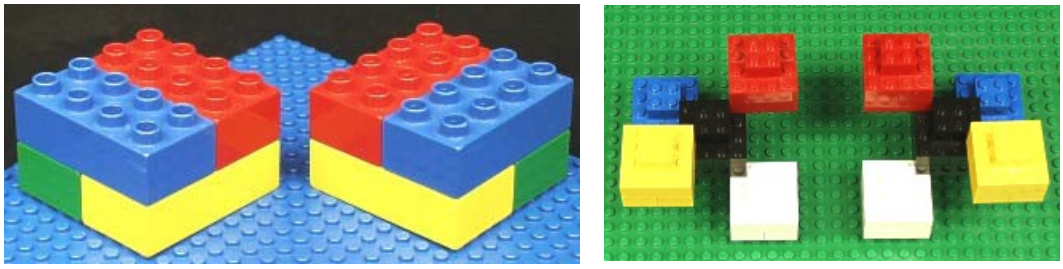


Figure 1.18 – Chiral structures using (left) 2x4 bricks or (right) clusters of two 2x2 bricks and four 2x4 bricks.

Chapter Two - Probing the Structure of Materials at the Nanoscale

Building or disassembling an instrument built from a familiar material such as LEGO® bricks provides a revealing view of the instrument and the principles behind it.

NOTE: LEGO® brick dimensions will often be described by numbers of pegs on their top surfaces. For example, a 2x4 brick is 2 pegs wide and 4 pegs long.

2.1 - Scanning Probe Microscopy

Scanning probe microscopy (SPM) is a method for mapping surface forces of materials on the atomic scale. By mapping these forces, much can be learned about the surfaces of materials, where many interesting and complex phenomena occur. For example, many chemical reactions involving solids are dependent on the nature of their surfaces. Scanning probe microscopy includes the methods of atomic force microscopy (AFM), magnetic force microscopy (MFM), and lateral force microscopy (LFM). Most force microscopy techniques are variations of the same basic principle, illustrated in Figure 2.1. Forces between the surface and a cantilever tip cause the tip to deflect up and down. Deflection of the cantilever shifts the position of a laser beam that reflects off the top of the cantilever onto a photodiode array. The movement of the beam between the photodiodes is used to calculate the cantilever deflection.

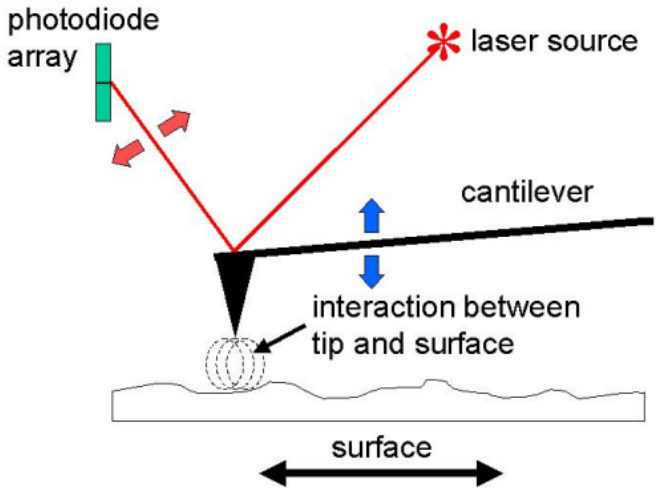


Figure 2.1 - The general principle behind force microscopy: Forces between the surface and the cantilever tip cause the tip to be deflected upward and downward. Deflection of the cantilever shifts the position of a laser beam that reflects off the top of the cantilever onto a photodiode array. The movement of the beam is tracked by the photodiodes and used to calculate the cantilever deflection.

Figure 2.2 shows a model of an atomic force microscope built from LEGO® bricks. The AFM contains a laser pointer and a cantilever with a triangular LEGO® probe on its underside and a mirror atop it. As in a real AFM, the cantilever is held in place and the surface is moved back and forth underneath the probe. In this model, the cantilever tip is

in physical contact with the substrate, so the pegs on the LEGO® substrate surface can be taken to represent a square array of surface atoms. The interaction between the probe tip and the surface results in deflection of the cantilever. Light from the pocket laser reflects from the mirror on the cantilever and shines onto a wall or screen. The farther the wall is from the AFM, the more the cantilever deflection will shift the beam spot on the wall.

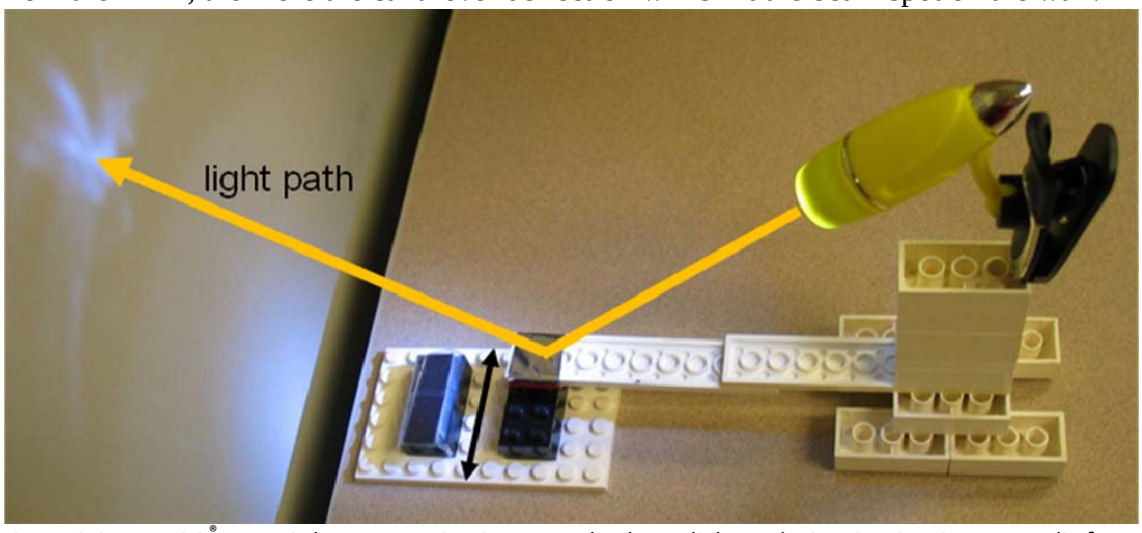


Figure 2.2 - A LEGO® AFM. Substrate motion is perpendicular to light path. See Section 2.1 Appendix for building instructions.

Modification of the model by addition of LEGO® magnets or other magnets converts it to a magnetic force microscope model, Figure 2.3. Here, the refrigerator magnet at the end of the cantilever interacts with a refrigerator magnet taped to the LEGO® surface to alternately attract and repel the cantilever.

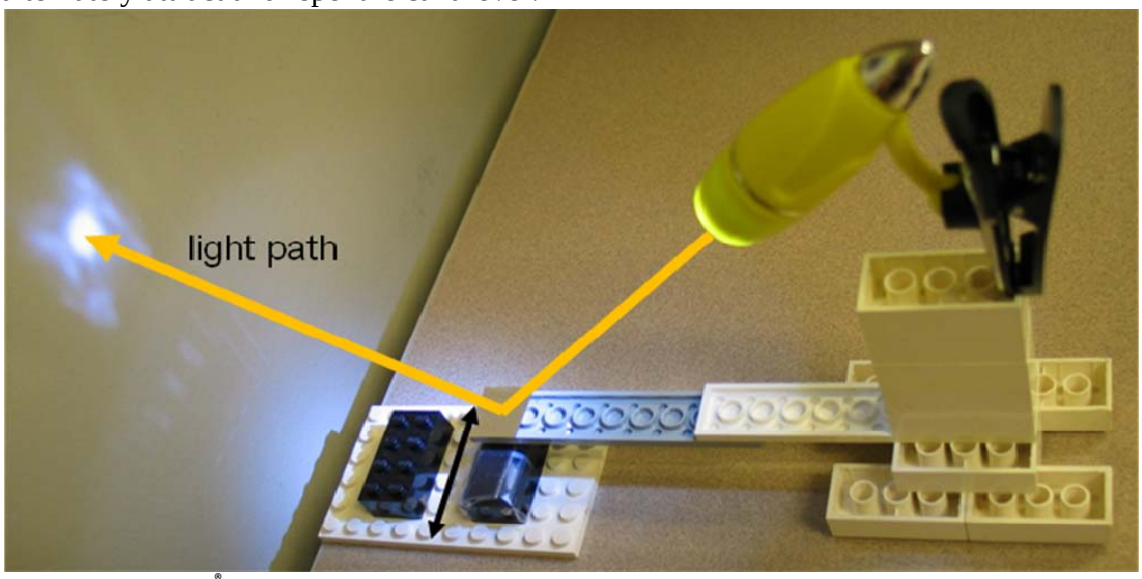


Figure 2.3 – A LEGO® MFM. Substrate motion is perpendicular to light path. See Section 2.1 Appendix for building instructions.

2.2 – Charge-Coupled Devices

A charge-coupled device (CCD) is a camera that produces digital images instead of conventional film images. The digital format allows the images to be manipulated by a computer, which can electronically sharpen, modify, or copy them.

CCDs are used to take pictures of very faint stars, and to make accurate measurements of position and therefore of speed and acceleration. They also serve as detectors in X-ray diffraction experiments, which provide information on the relative positions of atoms in materials and the sizes of nanoscale particles. In each case, the large detection area allows a great deal of information to be collected simultaneously.

In filmmaking, CCD cameras are useful for adding special effects. Previously, scenes were shot on conventional film and then scanned into a computer. This process is slow, and image quality is lost in the process. With a CCD, the scene is placed directly onto a computer for editing.

A CCD relies on semiconductor properties for its operation. Basically, photons of certain frequencies of light (electromagnetic radiation) strike a layer of silicon, breaking electrons away from chemical bonds. A CCD collects and counts these electrons to determine how many photons were absorbed by the silicon.

Every CCD starts with a backing of some sort, usually glass. The backing is then covered with metal electrodes, as shown in Figure 2.4. The bottom row of electrodes is designated as the readout register.

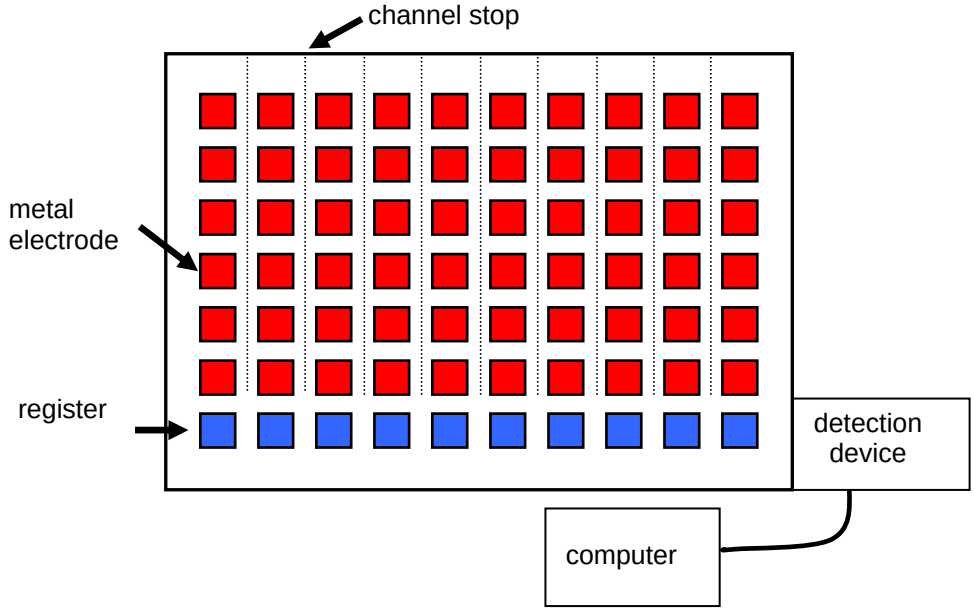


Figure 2.4 – Electrode array of a CCD.

A thin layer of silicon dioxide is placed over the electrodes, followed by two layers of silicon. The purpose of the silicon dioxide is to separate electrically the silicon from the electrodes and keep the electrons in the silicon. The two silicon layers contain small concentrations of other elements. This creates an electronic boundary called a p-n junction, allowing an electrical current to travel efficiently through the silicon. Between each column of electrodes in the silicon layer there is a channel stop, indicated by dashed lines in Figure 2.4. Channel stops prevent electrons from flowing horizontally across the CCD array. There are no channel stops in the readout register; in this row, charges are free to move horizontally to the detection device. A cross section of a portion of a CCD is shown in Figure 2.5.

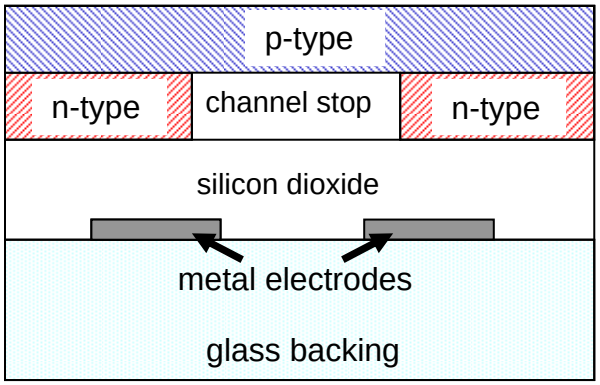


Figure 2.5 – Cross section of a portion of a CCD.

Each CCD is divided into many groups of electrodes called pixels. The exact number of pixels depends on the individual pixel size and the cost of the array. The CCD cannot differentiate between a photon of red or blue colored light, because it can only count numbers of electrons. In order to provide color images, the silicon above a group of electrodes is covered with red, green, and blue colored filters and combined to make a single color pixel.

Many photons of light are absorbed by the silicon layer as they enter the CCD. Each absorbed photon breaks electrons away from chemical bonds. Next, all of the collected electrons are sequentially moved to the detection device where they are counted. This is accomplished by changing the charge of the electrodes under the silicon layers in a timed, sequential manner.

To illustrate using Figure 2.6, electrodes 2 and 5 are initially positively charged (the red electrodes in the left-hand part of diagram) and therefore collect all the electrons photogenerated around them. Next, electrodes 3 and 6 gradually begin to acquire positive charge while 2 and 5 gradually become negatively charged. This causes the electrons to move to electrodes 3 and 6 (Figure 2.6, middle). Then, electrodes 1, 4, and 7 gain positive charge while 3 and 6 become negatively charged This causes the electrons to move once more (Figure 2.6, right-hand part). The electrons from the bottom-most pixel (pixel #2) are now in the readout register, electrode 7.

The readout register now begins to deliver the electrons along the bottom of the CCD to the detection device by the same process of varying the charge of its electrodes. The detection device counts the number of electrons by applying a known voltage across the final electrode. (The final electrode is located inside the detection device, not on the CCD array.) The voltage will increase slightly as electrons arrive from the CCD. By subtracting the background voltage, the voltage from the CCD electrons can be found. The number of electrons can then be calculated by a computer.

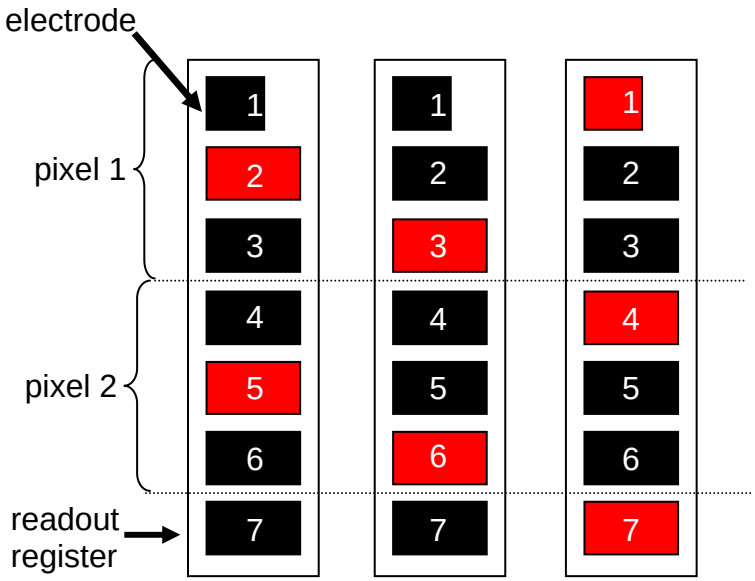


Figure 2.6 - An illustration of moving electrons by changing charges within a single column of electrodes in a CCD.

A LEGO® model of a CCD is shown in Figure 2.7. The table tennis ball simulates an electron while the colored bars simulate the electrodes. In this model, bar height is inversely proportional to voltage: as the bar drops down the voltage becomes more positive. By pushing and releasing the levers in sequence the bars drop and rise in sequence, moving the ball to the ramp at the left that represents the readout register.

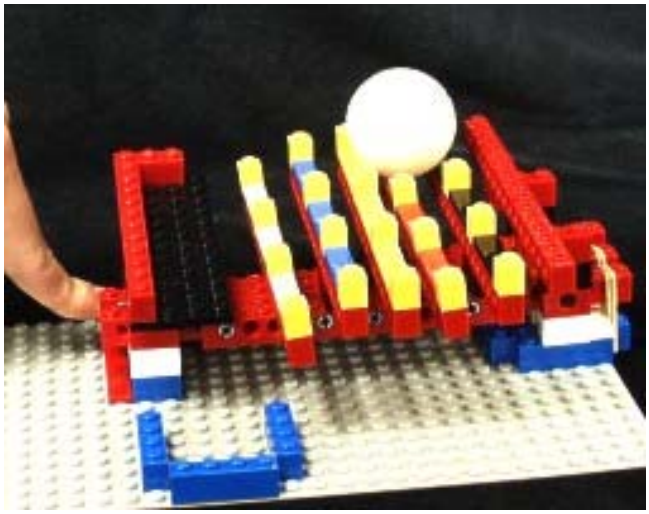


Figure 2.7 - This CCD model demonstrates how changing charge on the electrodes causes the electrons to move. See Section 2.2 Appendix for building instructions

2.3 - Photometry

Photometry is a widely used tool for characterizing the electronic structure of materials and determining the amount of matter present. Electrons are the "glue" that holds atoms together at the nanoscale, and their properties often become evident through the interaction of matter with light.

Photometry refers to qualitative and quantitative aspects of the interaction of matter with light. Qualitatively, absorption of light corresponds to inducing electronic transitions between energy levels of an atom, ion, molecule or material. The separation in energy levels corresponds to the portion of the electromagnetic spectrum that is absorbed. This technique is thus used for solid materials as well as for liquids and gases. Quantitatively, a larger path length and/or higher concentration of matter will lead to absorption of a greater fraction of incident light.

The essential components of a photometer are a light source, a sample, and a light detector, shown in Figure 2.8. Most photometers also contain some means to select a relatively narrow spectral region of light such as orange light. The detector measures the intensity of the light that is reaching it. Without the sample in the light beam to absorb some of the light, the light intensity reaching the detector is defined as I_O. When the sample is in place to absorb some of the light, the intensity of light reaching the detector is defined as I. Therefore the transmittance (T), which is the fraction of original light that passes through the sample, is defined as:

$$T = I/I_O$$

Another unit of measurement used in photometry is absorbance (A), defined as:

$$A = -\log T$$

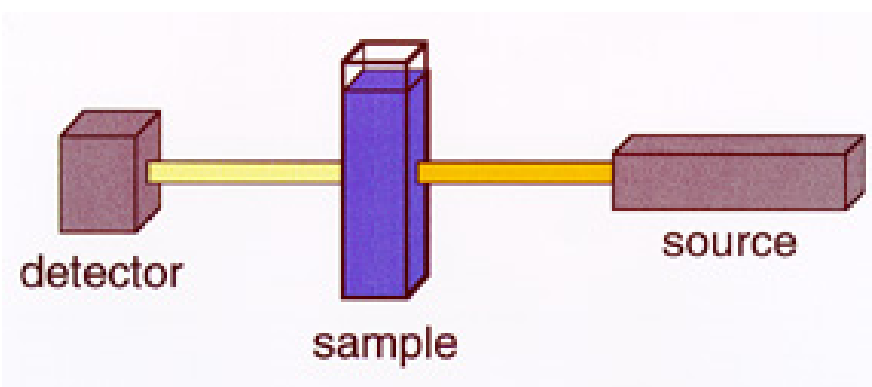


Figure 2.8 – General schematic of a photometer.

Figure 2.9 below shows a working photometer built from LEGO® bricks. It can be built or taken apart to provide an understanding of the basic principles of spectroscopy. This photometer may be built with light sources and sensors available through the LEGO®

Corporation. The sensor may be interfaced with a computer to read the light transmitted through the sample. The only non-LEGO® piece in this model is the sample cell, which consists of a conventional plastic spectrophotometer cuvette glued to a standard 2x2 LEGO® brick in order to fasten it to the LEGO® board underneath. Notice that this model also includes a shutter to regulate the beam intensity and shape. The components are placed in a casing to minimize stray light from other sources. The dummy sensor marks an alternate position for the light sensor.

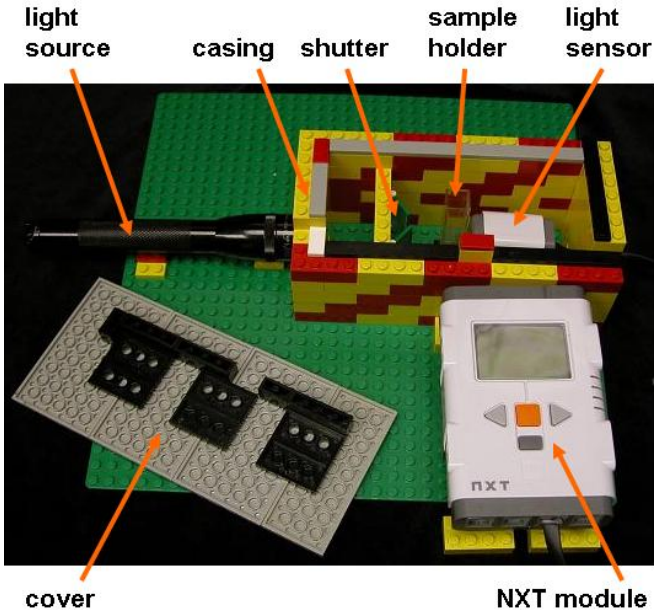


Figure 2.9 - A LEGO® photometer. See Section 2.3 Appendix for building instructions.

One way in which photometers may be used to find chemical concentrations is through a calibration curve. To make the calibration curve, the absorbances of a number of samples with known concentrations of chemicals are measured. These samples are called standards. The absorbances of these standards are plotted as a function of their known chemical concentration, resulting in a line or curve like that shown in Figure 2.10. When an unknown sample is measured, its absorbance may then be used to calculate its chemical concentration.

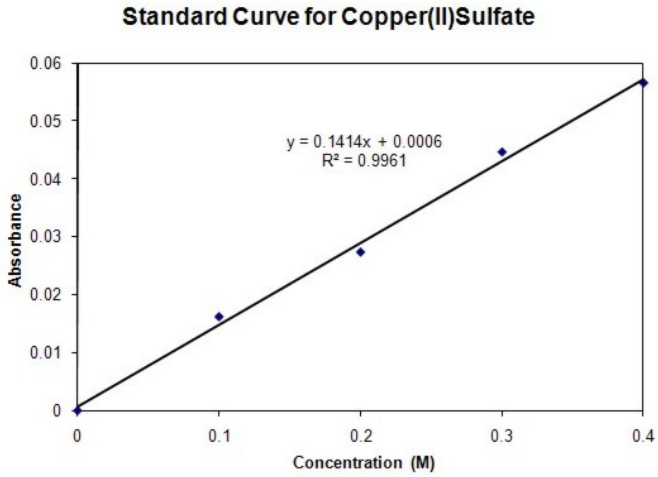


Figure 2.10 - A calibration curve. The points are calibration data used to construct the curve.

A calibration curve can be modeled with LEGO® bricks. Stacks of different numbers of bricks can be arranged in order of height. The height of each stack can be correlated to the different numbers of bricks. This can be plotted with height on the y-axis and number of blocks on the x-axis. Then when another stack (of a different color to signify that it is an unknown) is given to the students, they can see that it is the same height (y value) as the stack with the same number of bricks (x value). Examples of LEGO® graphs are shown in Figure 2.11. The left curve describes a linear graph and its use as a calibration curve. The middle curve describes a first-order decay, where each column of bricks is half the height of the previous column of bricks. This can be representative of processes such as radioactive decay, in which the concentration of a particular radioactive element decreases by a factor of two for constant time intervals (half-lives). The right curve describes an exponential growth, where each column of bricks is ten times the height of the previous column of bricks. This has been used as a demonstration of solution pH, in which each change in pH by one unit represents a ten-fold change in hydrogen ion concentration in solution.

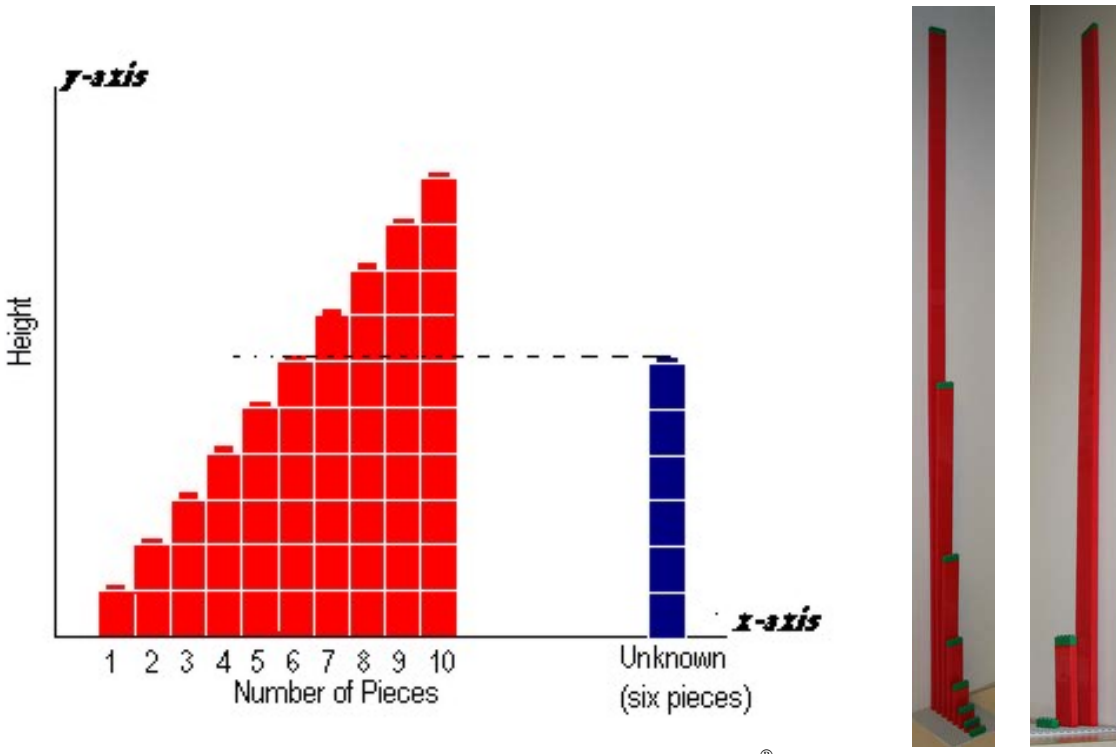


Figure 2.11 – (left) A linear calibration curve modeled with 55 1x1 LEGO® bricks. (middle) A curve of 255 1x4 LEGO® bricks describing first-order decay. (right) A curve of 111 1x4 LEGO® bricks describing exponential growth. The top bricks of the columns in the middle and right curves have different-colored bricks for visibility and the tallest column in each is taped to a wall for stability.

Different types of light measurements may be taken if the detector is in the 90° geometry, as shown in Figure 2.12. In this arrangement, the detector measures light leaving the sample at an angle of 90° from the source light beam. Therefore, the detector does not measure any light shining directly through the sample from the source. This geometry allows measurements of effects such as fluorescence and light scattering. These techniques may also use calibration curves such as the one shown in Figures 2.10 and 2.11, although the Y-axis data are light intensity rather than absorbance. The light

detector in the LEGO® model shown in Figure 2.9 above can be mounted in a 90° geometry by switching its position with the dummy sensor.

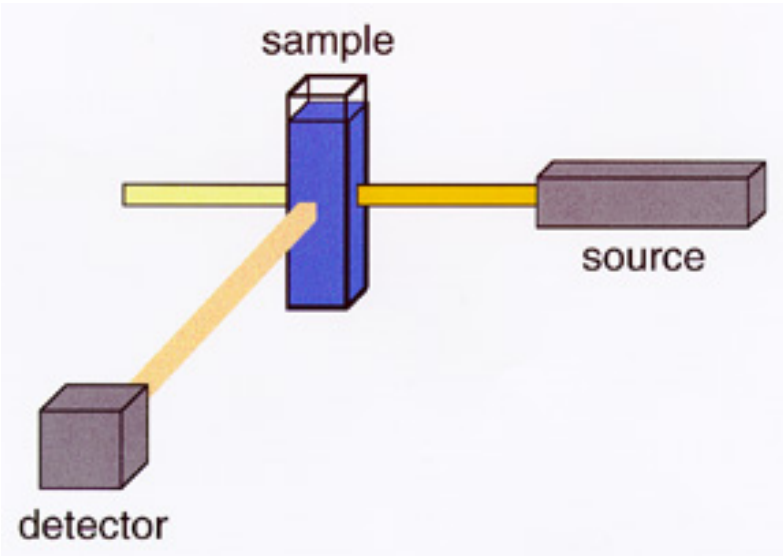


Figure 2.12 - The 90° geometry for light scattering measurements

One of the many uses of a photometer in a 90° geometry is turbidimetry, which measures turbidity, or cloudiness. When light passes between two substances (such as water droplets in air, or mud particles in water) some of the light is scattered. More particles provide more opportunities for light to pass between substances, and more light is scattered. Therefore, even though water and air are both transparent, light can be scattered so much by the air/water boundary of water droplets that it may be difficult to see on a foggy day. Turbidity also has environmental implications. When soil is washed into a waterway, the water can become turbid, affecting plants and animals. Turbidimetry may be used to monitor water cloudiness due to soil erosion.

2.4 – Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a technique used to determine the structures of chemical compounds. Many atomic nuclei have their own magnetic fields, as if they were tiny bar magnets. These magnetic nuclei are referred to as magnetic “spins”. When the magnetic nuclei are placed in the presence of a magnetic field, they will either align their nuclear spins with or against the magnetic field. By irradiating the nuclei with a pulse of electromagnetic radiation perpendicular to the magnetic field the nuclear spins will first align themselves with the pulse and then rotate in a plane perpendicular to the applied magnetic field. The frequency of this rotation, called resonance, is proportional to the strength of the applied magnetic field that the nucleus experiences. Isolated nuclei of the same element would all experience the same magnetic field and thus have the same resonant frequency. However, each nucleus in a chemical compound is in a slightly different magnetic environment because it is in a slightly different chemical environment. Therefore, magnetic nuclei in chemical compounds may experience different magnetic

fields and thus have different resonant frequencies. The detector in the NMR identifies the different resonances and translates them into a spectrum that allows the user to determine the chemical structure.
A simple model of a pulsed NMR experiment built with LEGO® bricks can be used to illustrate the idea of resonance. The swiveling magnets represent the nuclear spins, and the stationary magnetic array represents the applied external magnetic field. Adjusting the height of the stack of bricks upon which the swiveling magnets are placed can change the distance between the magnets. In particular, increasing the height of the stack of bricks decreases the strength of the stationary magnetic field felt by the swiveling magnets.

The mechanical analogy to NMR described in Figure 2.13 requires 10 flat face-poled LEGO magnets all in the same magnetic orientation, 5 swiveling face-poled magnets, and stacks of one to five conventional 1x1 bricks. Normally, the swiveling magnets will orient themselves in the same direction as the stationary magnets.

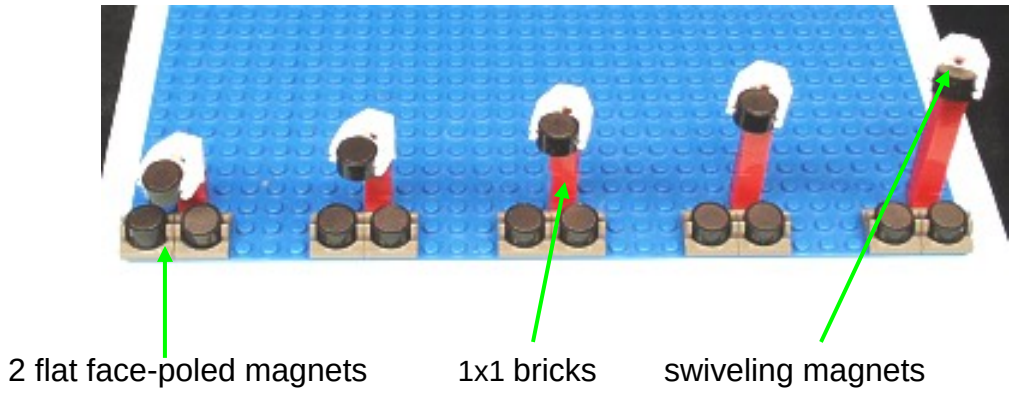


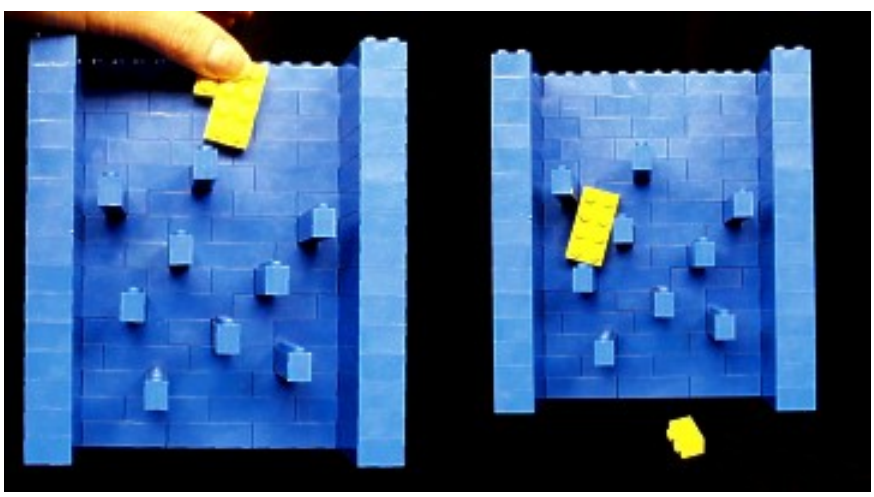
Figure 2.13 – Setup for the LEGO® pulsed NMR experiment.

Manually rotating the swiveling magnet 90° out of position represents a pulse of electromagnetic radiation that rotates the nuclear spins. When the rotated magnet is released, it will oscillate as it swings back into alignment with the stationary magnetic field. Swiveling magnets that are placed closer to the permanent magnetic array will have higher frequency oscillations as they realign with the stronger applied magnetic field. The oscillation of the swiveling magnets is analogous to the resonant frequency of the nuclear spins, which also increases as the applied magnetic field increases.

Figure 2.14 – "Pulsing" the LEGO® NMR experiment by pushing down on the magnet and releasing.

2.5 – Chromatography

Chromatography is a widely used technique for the separation of chemical components in a mixture. The technique involves moving the mixture, called the mobile phase, over or through a solid, high surface area material called the stationary phase. The stationary phase will slow the rate of flow differently for different chemical components in the mobile phase. Thus two components that are combined at the beginning of the process will leave the stationary phase at two different times. In the LEGO® model of this process, described in Figure 2.15, a column of stationary phase material is represented by a trough with the sides comprised of 2x8 bricks and the back 2x4 bricks. The packing material is represented by 1x8 bricks, the same length as the sides of the column, that are placed randomly along the trough. As you insert molecules, represented by different size bricks, into the top of the column, they are slowed down by the stationary phase. Larger bricks will slow down more and therefore come out of the column last. This is analogous to the adsorption and desorption of real species to the material of the stationary phase. A greater affinity for the stationary phase is modeled by an increase in size of LEGO® bricks. Some shaking of the column may be needed in order to remove all of the bricks from the column. Shaking can be analogous to pressure forcing the mobile phase through a real chromatography column. Along with many other uses, chromatography has been used to separate different sizes of nanoscale particles.



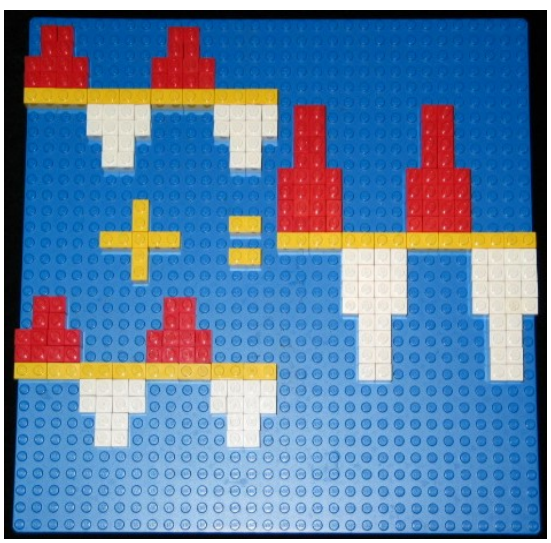
Type of LEGO® brick	Number of LEGO® bricks
2x4 bricks	77
2x2 bricks	24
2x3 bricks	18
1x8 bricks	9
1x1 bricks	2

Figure 2.15 – (left) Two LEGO® "molecules" at the top of a trough representing a chromatography column. (right) The smaller brick leaves the trough first.

2.6 – Diffraction and Wave Addition

A variety of methods for studying patterns in materials is based on the principles of diffraction. These methods are based on the scattering of waves from various locations within the structure of the material. These waves can be those of electromagnetic radiation, such as light or X-rays, or subatomic particles that have some wavelike

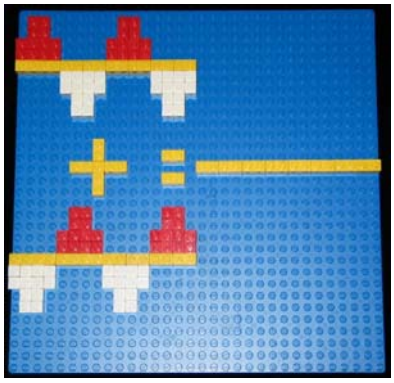
character, such as electrons and neutrons. The way the waves scatter from the material and interact with each other can be measured and used to elucidate the material structure. When two or more sets of waves cross paths, they combine together in ways that can produce more intense or less intense resulting waves, sometimes even canceling each other out. Figure 2.16 illustrates this principle with 1 peg x 1 peg bricks arranged on a flat base board. This arrangement uses the base board as a sort of graph paper and the bricks represent the ink for drawing graphs. The oscillating patterns at the left side of the board represent sets of waves that are crossing paths and will be added together. The yellow lines represent the center of the oscillation. On graph paper this would represent the x axis (y = 0) for each wave. The crests of the waves are shown with red bricks and are located above the yellow line. The troughs of the waves are shown with white bricks and are located below the yellow line. A wave crest and trough together constitute one wave. The distance along the x axis from a point on a wave to the same point on the next wave is called a wavelength. The distance between the height and depth of the wave is referred to as its amplitude. Figure 2.16 represents the combination of two sets of waves with the same wavelength and amplitude. These sets of waves are also "in phase" – the waves match crest to crest and trough to trough. The easy addition of bricks to the boards and their easy removal allows for a rather quick summing of the waves to produce the resulting wave pattern at the right side of the board. For each column of pegs in the left side sets of waves, add up the number of red bricks and subtract all of the white bricks. For example, the first column of pegs has four red bricks and no white bricks. Therefore the first column of pegs for the waves on the right side should have four red bricks. The sixth column of pegs has no red bricks and eight white bricks. Therefore the sixth column of pegs for the waves on the right side should have eight white bricks. Note that the resulting set of waves has the same wavelength as the originals, but double the amplitude. This summing of waves to produce waves of larger amplitude is called constructive interference.



Type of LEGO® brick	**Number of LEGO® bricks**
1x1 red bricks	96
1x1 white bricks	96
2x2 yellow bricks	30
1x1 yellow brick	1
32x32 baseplate	1

Figure 2.16 – Combination of two sets of waves that are "in phase" with each other, resulting a set of waves with double the amplitude.

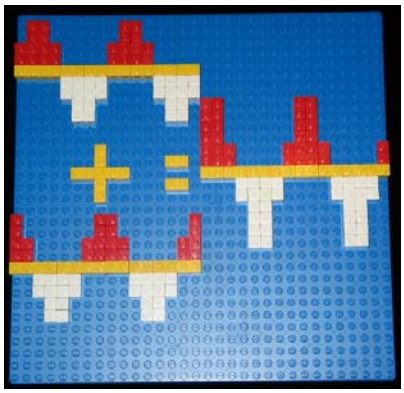
Figure 2.17 represents the combination of two waves with the same wavelength and amplitude that are also completely "out of phase" – the waves match crest to trough and trough to crest. These waves cancel each other out completely, which can be shown by counting the bricks. For example, the first column of pegs has two red bricks and two white bricks. Therefore the first column of pegs for the waves on the right side of the board should have no red or no white bricks. The sixth column of pegs has four red bricks and four white bricks. Therefore the sixth column of pegs for the waves on the right side of the board should have no red or no white bricks. Note that the resulting waves have no amplitude and therefore does not exist. This summing of waves to produce waves of smaller amplitude or to completely cancel each other out is called destructive interference.



Type of LEGO® brick	Number of LEGO® bricks
1x1 red bricks	48
1x1 white bricks	48
2x2 yellow bricks	30
1x1 yellow brick	1
32x32 baseplate	1

Figure 2.17 – Combination of two sets of waves that are completely "out of phase" with each other, resulting in the waves completely canceling each other out.

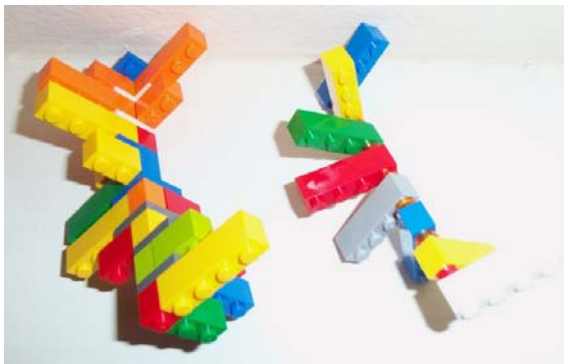
Figure 2.18 represents the combination of two waves with the same wavelength and amplitude that are only partially "out of phase" – the waves do not match completely nor cancel each other out completely, which can again be shown by counting the bricks. For example, the first column of pegs has six red bricks and no white bricks. Therefore the first column of pegs for the waves on the right side of the board should have six red bricks. The sixth column of pegs has no red bricks and six white bricks. Therefore the sixth column of pegs for the waves on the right side of the board should have six white bricks.



Type of LEGO® brick	Number of LEGO® bricks
1x1 red bricks	80
1x1 white bricks	80
2x2 yellow bricks	30
1x1 yellow brick	1
32x32 baseplate	1

Figure 2.18 – Combination of two sets of waves that are partially "out of phase" with each other, resulting in a new, different set of waves.

Waves that are not in the same plane can also be combined. Circularly polarized light can be considered to be the sum of two electric field waves at 90° angles to each other and partially out of phase with each other. The resulting light can be described as having a spiraling electric field. Figure 2.19 represents the combination of two waves that are at 90° angles to each other and partially out of phase.



Type of LEGO® brick	Number of LEGO® bricks
1x1 bricks	8
1x2 bricks	8
1x4 bricks	16
1x1 flat bricks	8
2x2 flat bricks	8

Figure 2.19 – Combination of two sets of waves that are at 90° angles and partially "out of phase" with each other (left), producing a spiral pattern (right).

Diffraction methods use waves to find the repeating arrangements of atoms in crystal structures (see Section 1). This is most commonly done by shining a shining a beam of X-rays at a crystal of material. When the X-ray waves encounter the atoms in the crystal they scatter in various directions. When waves scattered from different atoms encounter each other they can interfere constructively in some places and destructively in others to produce a diffraction pattern. This pattern of X-ray variation can be measured with detectors and can be used to calculate the positions of atoms in the crystal structure. Though X-ray diffraction is most common, other waves can be used to produce diffraction patterns. Figure 2.20 shows a visible light diffraction pattern produced by shining a laser through a structure containing regions of polymer spheres in a face-centered cubic arrangement. A relatively simple model of the face-centered cubic structure and its unit cell is described in the Section 1.2 Appendix.

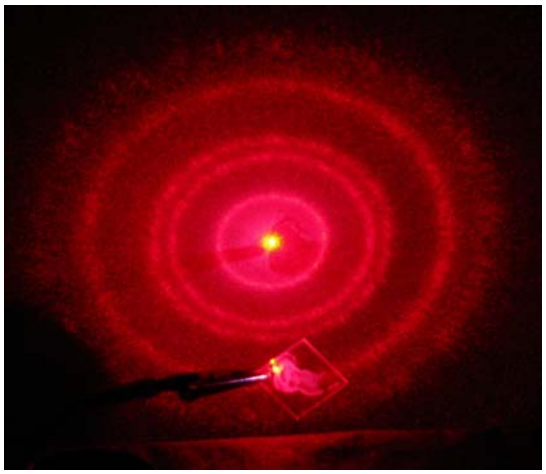


Figure 2.20 – Visible light diffraction from face-centered cubic arrangements of polystyrene spheres. The spheres are each about 3000 nanometers in diameter.

Often water comes to mind when waves are mentioned, and water has long been used in so-called wave tanks to demonstrate principles of diffraction. Figure 2.21 shows a wave tank made from LEGO® bricks in conjunction with a flat pan filled with water. The system uses long straight waves generated by oscillating a flat wall of LEGO® bricks that is dipped partway into the water. The waves produced by the paddle can be scattered by barriers made from LEGO® bricks. The barriers are made from bricks with their pegs oriented sideways, enabling them to be sunken more easily in water.

Figure 2.21 – (top) A wave tank made using LEGO® bricks and a flat pan filled with water. A long, straight wave can be produced by oscillating a flat wall of LEGO® bricks. The wall can be oscillated up and down by using a LEGO® machine or by hand. (bottom) Interference between sets of circular waves scattered from two gaps in the 2x4 LEGO® brick barrier. The water level is lower than the bricks oriented vertically but higher than the bricks in the gaps that are oriented horizontally.

2.7 - Scanning Electron Microscopy

An electron microscope uses electrons, rather than light (photons), to obtain magnified images of a sample. There are many different electron microscopy techniques, including scanning electron microscopy (SEM). In SEM, a beam of electrons is scanned back and forth across a surface, producing a variety of electrons and X-rays that can be used to analyze the structure of that surface. One of the most common SEM techniques involves detecting electrons that have been bumped away from sample atoms by the microscope electron beam. These secondary electrons, as they are called, are produced both at the surface and under the surface of the sample. On areas of the sample that face the electron beam, only the secondary electrons produced at the surface escape the sample and are detected. At the edges of the sample that do not directly face the electron beam, the secondary electrons produced under the surface can also escape the sample and are also detected. Increased numbers of electrons reaching the detector in the SEM become brighter areas of the sample image that the microscope produces. The resulting sample images show features that appear to be lit from the side – brighter at their edges than where they face the electron beam.

This edge effect can be modeled with simple household items:

- firm, flat surface (like a table top)
- white crayon
- black paper
- adhesive tape
- flat LEGO® bricks

Tape the bricks to the flat surface to prevent the bricks from shifting. Place the paper over the bricks. Rub the white crayon lightly over the paper over the area where the bricks are taped. The crayon marks will cover all of the paper to some extent, but will be heaviest at the edges of the object under the paper, similar to secondary electron emission being greatest at the edges of samples in the SEM, Figure 2.22.

In this demonstration, the piece of white crayon represents the electron beam of the microscope scanning across a sample surface. The crayon marks on the paper represent the secondary electrons produced by the sample, and the image on the black paper resembles an image that would be produced by an electron microscope.

Figure 2.22 – (top) Flat LEGO® bricks taped to a flat surface in the pattern of the letters “FNT”. (bottom) White crayon marks rubbed on the black paper picks up the pattern of the pegs.

Chapter Three – Structure-Property Relationships at the Nanoscale

This chapter links the atomic and molecular arrangement of matter to physical properties such as strength, stiffness, and magnetic properties.

NOTE: LEGO® brick dimensions will often be described by numbers of pegs on their top surfaces. For example, a 2x4 brick is 2 pegs wide and 4 pegs long.

3.1 - Polymer Cross-linking

Polymers include all the plastics we are familiar with in everyday life. They are materials that are composed of large molecules that, in turn, are composed of molecular building blocks called monomers, Figure 3.1. The monomers can repeat in a variety of ways to build up polymers of varying overall size.

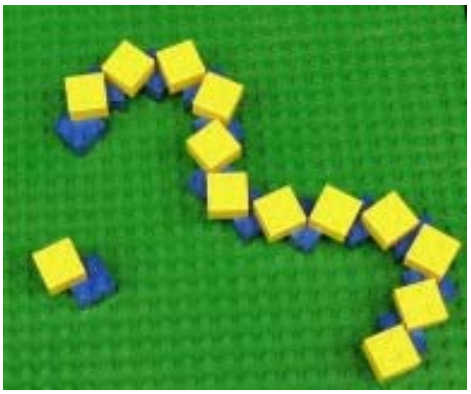


Figure 3.1 – Representations of a monomer (left) and a polymer (right) using 13 yellow and 13 blue 2x2 LEGO® bricks.

Most LEGO® bricks are composed of the polymer acrylonitrile butadiene styrene, also known as ABS. Each repeating unit of the polymer ABS has the structure shown in Figure 3.2, and n represents the number of such units that are bonded together to form a polymer chain.

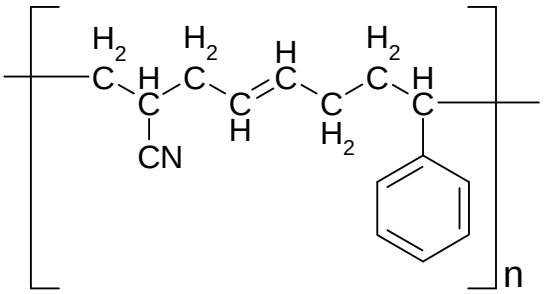


Figure 3.2 - Structure of acrylonitrile butadiene styrene (ABS), the polymer building block from which most LEGO® bricks are prepared.

Polymers have a wide range of properties that are dependent on their molecular structure. One structural quality of a polymer that can drastically affect its behavior is cross-linking. Cross-linking in polymers can be easily modeled with LEGO® bricks. Linear rows of linked LEGO® bricks, Figure 3.3, left, represent unlinked chain-like polymer molecules. Note that these chains can move relative to each other with comparative ease. However, linking the LEGO® chains with additional LEGO® bricks, Figure 3.3, right, makes the structure more rigid.

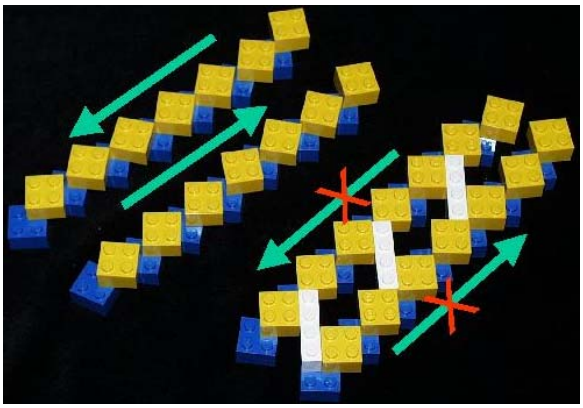


Figure 3.3 - (left) Unlinked chains of seven yellow and seven blue 2x2 LEGO® bricks can slide past each other in the direction indicated by the arrows. (right) Chains of bricks cross linked by the three white 1x4 bricks cannot slide past each other, as indicated by the red "x"s through the arrows.

In the same manner, polymers that are composed of cross-linked polymer chains are often more rigid than similar, non-cross-linked polymers, as illustrated in Figure 3.4. The higher number of cross-links (shown in red) in the polymer at the right of the illustration enable it to be more rigid and less deformed by an applied stress, which is represented in the each figure by an identical weight.

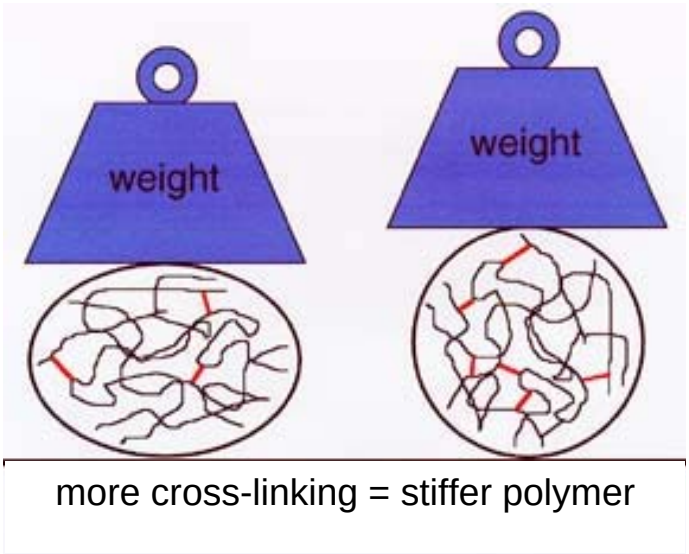


Figure 3.4 - Increased cross-linking in the right-hand polymer sample compared to the left-hand sample (cross-links shown in red) results in a stiffer polymer.

This LEGO® model of polymer structure may also be used to illustrate biodegradable polymers, in which polymer structures, such as in Figure 3.3, right, contain environmentally-sensitive groups (such as light-sensitive groups) that can break. When these links break, the polymer degrades into smaller pieces (Figure 3.3, left).

The website associated with this book contains building instructions for a number of polymer models. These can be accessed from the page called LEGO® Molecular-Scale Models, http://mrsec.wisc.edu/Edetc/LEGO/index.html.

3.2 - Poisson's Ratios

When most objects are stretched, they become thinner in cross section. Examples include rubber bands and chewing gum. This property of materials may be described by the Poisson's ratio, symbolized by μ (mu).

$$\mu = \frac{\text{\% decrease in width}}{\text{\% increase in length}}$$

Poisson's ratio can be demonstrated with the LEGO® lattice shown in Figure 3.5. The rectangular piece of paper behind the lattice is used as a size reference.

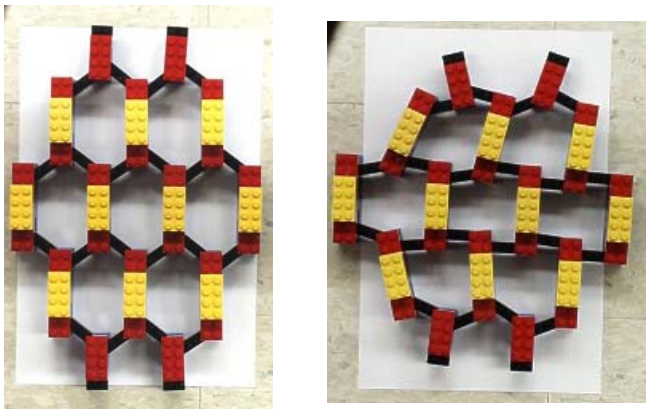


Figure 3.5 - A LEGO® lattice with a positive Poisson's ratio: (left) unstretched and (right) stretched horizontally. Note that the lattice contracts vertically (in a direction perpendicular to stretching).

In the LEGO® lattice in Figure 3.6, the structure has a negative Poisson's ratio: The structure expands in both directions as it is stretched. The difference lies in the shape of the holes or pores in the structure. Whereas the structure in Figure 3.5 has rather open holes, the structure in Figure 3.6 has somewhat collapsed holes. When this latter structure is stretched, the holes are pulled open, expanding the entire structure.

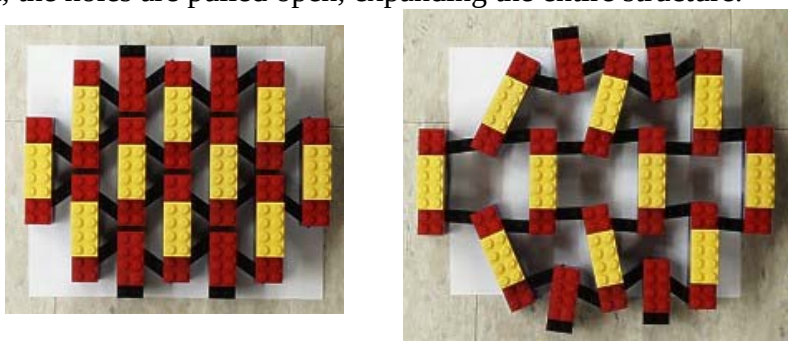


Figure 3.6 - A LEGO® lattice with a negative Poisson's ratio: (left) unstretched and (right) stretched horizontally. Note that the lattice expands vertically (in a direction perpendicular to stretching). Building instructions are available in Appendix 3.2.

This experiment is a compelling demonstration of how changes in structure can drastically affect function. A similar effect can be observed with the Hoberman spheres that are sold as toys, Figure. 3.7.

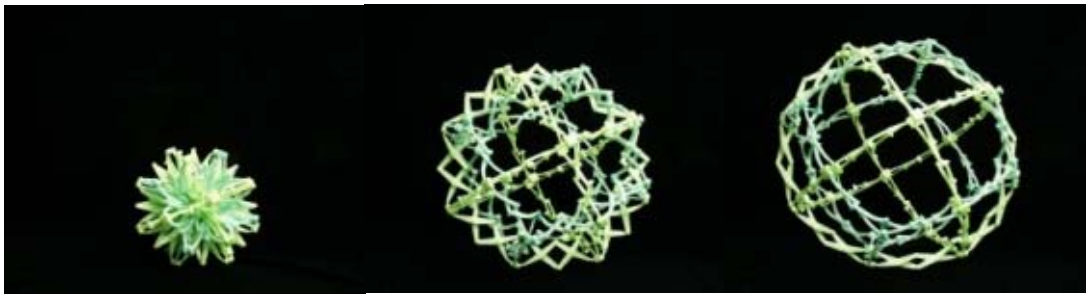


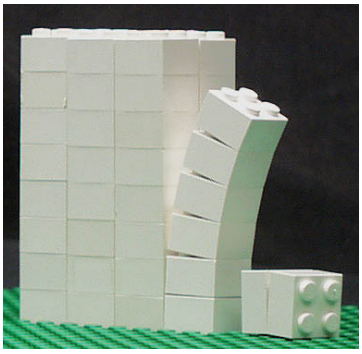
Figure 3.7 - A Hoberman sphere.

These LEGO® structures have polymer analogs. Polyurethane foam normally has a positive Poisson's ratio when it is stretched. However, when the foam is compressed, the pores in the foam collapse. Changing the structure of the foam (by compressing the foam with force applied from all sides and heating it until the collapsed pores are permanently collapsed) will change the function of the foam. When the altered foam is stretched, the collapsed pores expand, causing the entire foam structure to expand. Therefore this treated foam (referred to as "re-entrant foam") now has a negative Poisson's ratio. Negative Poisson's ratios have been observed in some metals and at least one silicate structure. In contrast to the polyurethane foam, changes in these materials take place at a much smaller, nanoscale level.

3.3 - Silicates

Silicates and aluminosilicates are large classes of minerals found in many forms throughout the earth's crust. The variety of minerals in these classes is based on building units of silicate ions, SiO_4^{4-} (Aluminosilicates have some of their silicon atoms replaced with aluminum atoms, leading to units having the formula AlO_4^{5-}). These ions are shaped like tetrahedra with the Si or Al at the center of the tetrahedron and the oxygen atoms at the four corners of the tetrahedron. These tetrahedral units can connect at their corners to form chains, rings, sheets, and three-dimensional structures. Though LEGO® bricks are not tetrahedral, they can be used as a simple representation of some silicate and aluminosilicate structures. Note that in this section, the bricks do not represent specific atoms as in Section 1.2; rather, they can be taken to represent groups of atoms.

Asbestos-type minerals consist of silicate chains arranged parallel to each other. The interactions between the chains are relatively weak, resulting in a fibrous structure. This fibrous structure, combined with the high heat resistance that is typical of silicates and aluminosilicates, has led to the use of asbestos as insulation. The silicate chains of asbestos minerals can be represented by stacks of single LEGO® bricks. Several stacks placed together are readily peeled away from one another, just as asbestos fibers may be peeled from the bulk mineral.



Note: Asbestos is known to cause lung disease. Proper safety precautions must be taken when handling this substance.

Figure 3.8 - (left) Asbestos fibers. (right) A LEGO® model of the asbestos structure made from towers of eight 2x2 bricks. Note that the towers can peel away from each other to model the fibrous structure of asbestos.

Mica and clay-type minerals consist of aluminosilicate sheets arranged parallel to each other. The interactions between the sheets are relatively weak, allowing mica minerals to be peeled or split into flat sheets. Large, transparent sheets of mica were once used as stove windows. Vermiculite, a mica-type mineral, is "popped" like popcorn (due to the evaporation of water trapped between its sheets), resulting in a fluffy structure used as packing material and insulation. The weak interactions between the aluminosilicate sheets allow the sheets to slide past each other in some cases, resulting in the slippery feel of talc and wet clay.

The aluminosilicate sheets of mica and clay-like minerals can be represented by walls of single LEGO® bricks. Several walls placed together are readily peeled away from one another, just as mica sheets may be peeled from the bulk mineral.

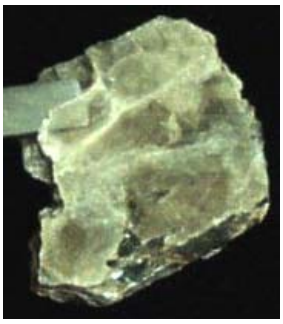
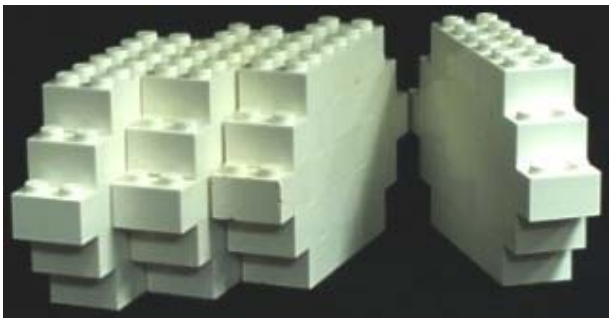



Figure 3.9 - (left) A mica mineral. (right) A LEGO® model of the mica structure made from brick walls of 19 2x2 bricks. Note that the walls can peel away from each other to model the sheet-like structure of mica.

Zeolites are complex, three-dimensional aluminosilicate structures that are often described as nanoporous solids because of the nano-sized pores present therein. These minerals can contain channels and empty spaces throughout their volumes, resulting in a porous, high surface area structure. The channels can trap specific molecules, leaving other molecules outside. Applications for such chemical selectivity have led to the synthesis of many artificial types of zeolites. These aluminosilicates can be used as ion

exchangers, molecular sieves, and catalysts. The channeled aluminosilicate structure of zeolites can be represented by three-dimensional structures of LEGO® bricks.

Figure 3.10 - (left) A zeolite mineral. (middle) A LEGO® model made from 40 2x2 bricks of a three-dimensional structure that is reminiscent of a zeolite, which features three channels, all perpendicular to each other. (right) The layers used to produce the LEGO® structure.

3.4 – Metal Deformation

When metals deform under applied pressure (e.g. when a metal is bent), sheets of atoms slide past each other. The interface along which these sheets slide are called slip planes. Relatively flat sheets of atoms move past each other more easily than sheets which are wrinkled or distorted. In other words, metals that contain many defects in their crystal structure are less easily deformed than metals with relatively few defects. This process can be demonstrated with a square array of 2x2 LEGO® bricks, Figure 3.11.

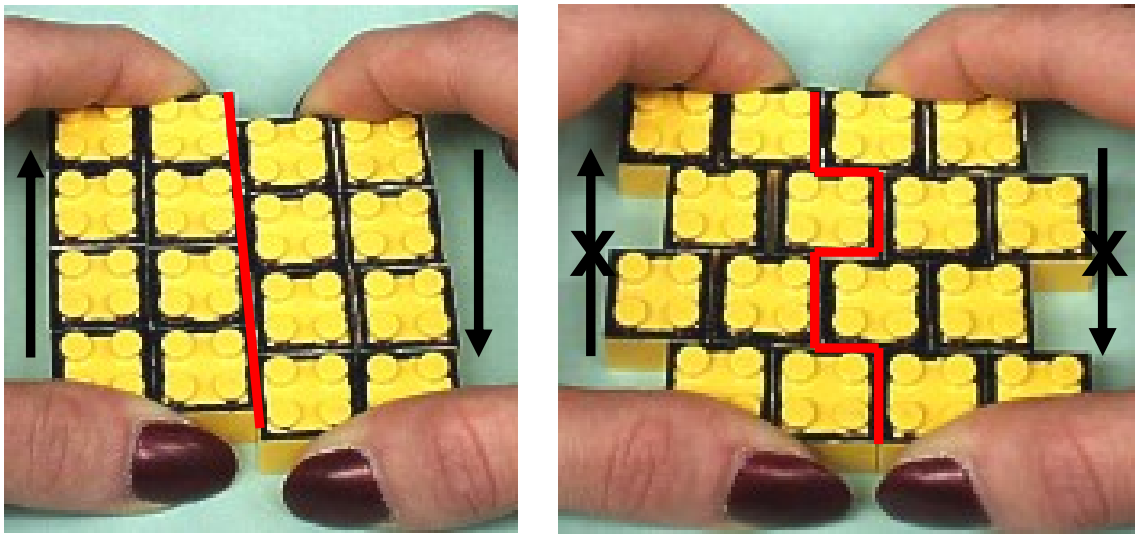


Figure 3.11 - (left) Slip plane motion between close-packed planes in regular structure represented by 16 2x2 bricks. (right) Slip plane motion is restricted between non-close-packed planes in distorted structure.

Researchers are trying to control the amount of defects in metals at the nanoscale level in order to control how easily the metals can be deformed, and therefore the hardness of the metals.

3.5 – Composites

A composite is a substance composed of two or more materials with different base structures combined in such a way that the end product has different properties than either of the parent materials. This is not exactly the same as an alloy or compound. Alloys and compounds are composed of two or more materials combined so that the materials form one new structure. A composite is two distinct structures blended together. The reason for combining two or more materials is that the resulting material has better properties than either parent material.

The reinforced concrete found in bridges and buildings is an example of a composite material. The steel rods augment the cement base structure to produce a material that is stronger than either parent material would be by itself. The iron bars and surrounding concrete are still distinct recognizable structures. They do not form one new material as they would in an alloy or compound. In the aerospace industry, composites are used to provide materials with comparable strengths at much lower densities. This reduces the weight of the aircraft and improves fuel efficiency. Automobiles employ many composite materials. Composite bodies reduce rusting effects and composite dashboards improve safety. Composites are also being developed using nanoscale components.

LEGO® bricks may be used to demonstrate composite materials. Suppose Material A is composed of structures like those shown in Figure 3.12. You could combine these structures as shown to form a beam, but it would not be very strong. It would deform and break easily.

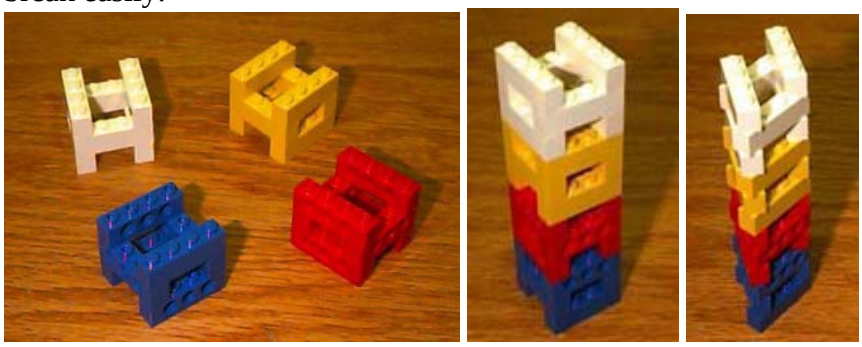


Figure 3.12 – (left) Units of Material A, each made from six 1x4 bricks. (middle) A beam of Material A. (right) A distorted beam of Material A.

You could make a beam out of just Material B as shown in Figure 3.13, but it would not be very strong either.

Figure 3.13 – (left) Beam of Material B made from three 2x8 bricks. (right) Distorted beam of Material B.

Using a combination of Materials A and B, you could build a composite material such as the one shown in Figure 3.14. As you can see from the comparison of the composite structure and the Material A structure, the composite is much stronger.

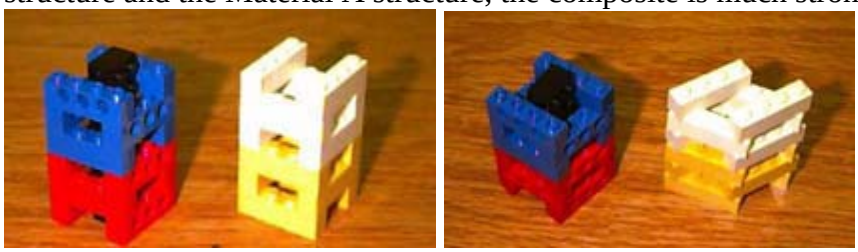


Figure 3.14 – (left) Composite beam and beam of Material A. (right) Slightly distorted composite beam and highly distorted beam of pure Material A.

3.6 - Giant Magnetoresistance

Giant magnetoresistance (GMR) is a property in which a magnetic field affects how well a material conducts electricity. Read heads in computer hard drives are made out of GMR materials due to the increased magnetic sensitivity of these heads over older inductive read head technologies.

One type of GMR material, called a magnetic multilayer material, is composed of alternating layers of ferromagnetic material and nonmagnetic metals, each having thicknesses on the nanoscale. In ferromagnetic materials, the spins from unpaired electrons align along one of two possible directions to give the material a total magnetic moment, which is the sum of the magnetic fields from the individual electron spins.

When the ferromagnetic and non-magnetic layers are of nanoscale thickness, the electron spins in alternating ferromagnetic layers spontaneously align antiparallel to one another (in opposing directions - Figure 3.15, left). When a magnetic field is applied, it causes the total magnetic moments of the ferromagnetic layers to realign in the direction of the applied magnetic field (Figure 3.15, right).

An electron moving through a ferromagnetic material (a conduction electron) passes through more easily if it encounters electron spins oriented in the same direction as its own spin orientation. In the antiparallel spin configuration that exists before a magnetic field is applied, any conduction electron would encounter a layer with electron spins pointed in the opposite direction. The conduction electrons are preferentially scattered under these conditions, leading to higher electrical resistance. In contrast, when the magnetic field aligns the magnetic moments in the multilayer in the same direction, conduction electrons travelling through the material with the same spin orientation as the magnetic moments in the material undergo less scattering, leading to lower electrical resistance, as shown in Figure 3.15.

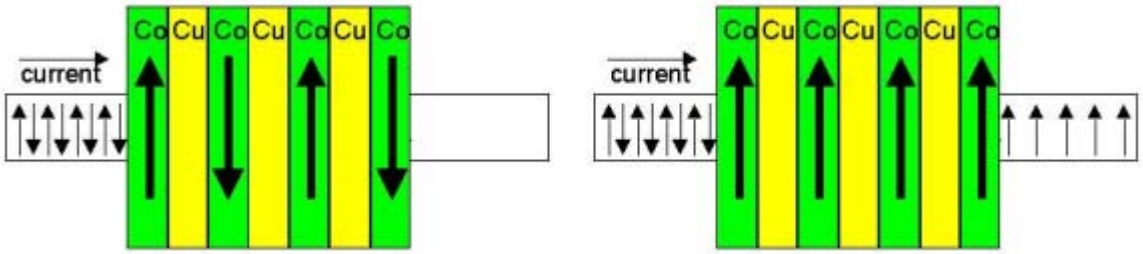


Figure 3.15 – (left) Electrical conduction of multilayered magnetoresistive structure without an applied magnetic field. (right) Electrical conduction of the structure when an applied magnetic field aligns the spins within the structure. The small arrows represent spin orientations of the conduction electrons and the large arrows represent the preferred alignment of the electrons in the nanoscale multilayer.

A multilayered magnetic structure can be built with LEGO® bricks. This structure uses LEGO® magnets attached to rotating LEGO® units. Without the influence of any outside magnetic field, the units on the axle will all line up in opposing directions. Each unit represents the magnetism of a ferromagnetic layer in the real structure with nonmagnetic intervening layers being the air gaps between the magnets. When the units are all aligned antiparallel to each other, holes in the units do not line up, so light (representing electrical current) cannot pass through the material (Figure 3.16, left). If a strong neodymium iron boron magnet is placed under the structure, its magnetic field forces the units to align magnetically. When the units are in alignment, the holes are also in alignment and light can pass through (Figure 3.16, right).

Figure 3.16 – A LEGO® magnetoresistance model without (left) and with (right) the influence of an applied magnetic field. The strong neodymium iron boron magnet, under the platform at right, should not be brought too close to the magnetic units or else it could pull the units apart. The laser light represents electrical current. Assembly of this model is described in Appendix 3.6.

3.7 – Plasmon Resonance

The highest energy electrons (the valence electrons) of atoms inside a metal are able to move freely throughout the metal. This collection of delocalized electrons interacts with the metal atoms to hold the metal together and known as a metallic bond. Plasmons are waves in this collection of mobile electrons that are produced when large numbers of these electrons are disturbed from their equilibrium positions. Within metal nanoparticles, these electron charge oscillations are known as localized surface plasmons (LSPs). The LSPs are produced when the nanoparticles absorb light of the right energy. The energy of light required to produce LSPs depends on a number of factors, including the sizes and shapes of the particles. Generally, as the particle size increases, the energy of light required to initiate a plasmon decreases. Therefore, larger particles absorb lower

frequencies or longer wavelengths of light. This can be represented in an abstract manner with LEGO® bricks by dropping them onto hard, flat, smooth surface and listening to the sound that they produce. For example, drop one 2x2 LEGO® brick onto a countertop from a height of a few centimeters; the sound that the brick makes represents the resonant frequency of that brick. The brick represents a nanoparticle; the collision with the countertop represents light striking the nanoparticle. As more bricks of the same size are stacked onto the original brick, the collision sound gets lower, which represents a shift to a lower sound frequency or longer sound wavelength. Therefore, by dropping stacks of one to six bricks, representing nanoparticles of different sizes, onto the same surface from the same height, one can observe and hear the sound frequency decreasing as the stacks get larger, Figure 3.17. To help reinforce the analogy between sound and light frequencies and wavelengths, the larger brick stacks (which ring at lower frequencies) are built with more reddish colors (corresponding to lower light frequencies).

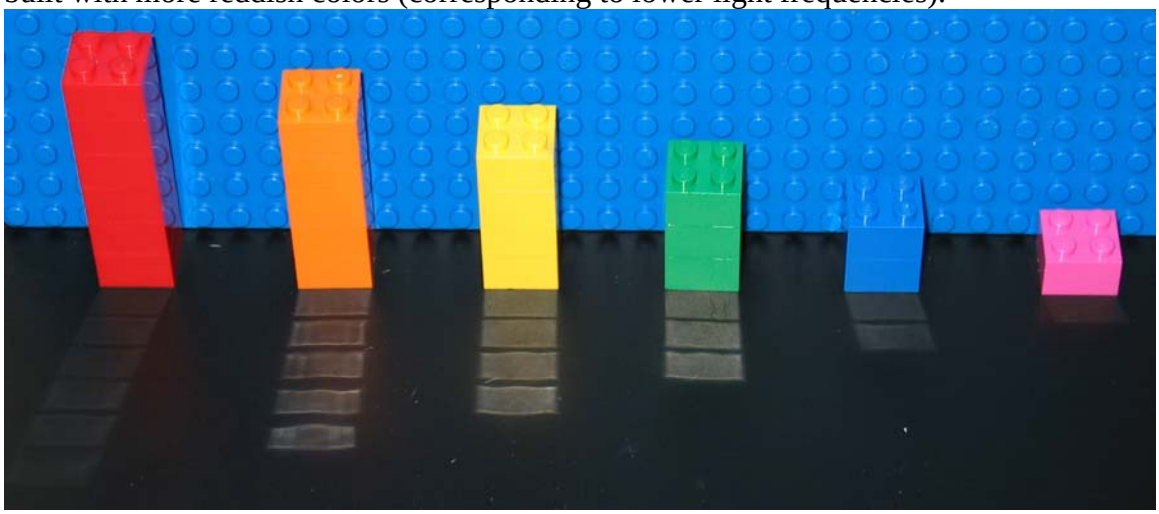


Figure 3.17 - Stacks of one to six bricks, representing nanoparticles of different sizes, which can dropped onto hard surfaces to represent light producing plasmons within the nanoparticles.

It should be stressed that the frequencies of light discussed above are ABSORBED by the nanoparticles. The colors that the nanoparticles actually appear to be are often the complement of the color absorbed. For example, gold nanoparticles, which tend to absorb green light, often appear to be red when viewed in white light. In addition to green and red, other complimentary colors include blue and orange, and violet and yellow. These complimentary colors can be depicted with a color wheel, Figure 3.18, which is effectively produced by turning the visible light spectrum into a circle. The color wheel is also used to describe color relationships for non-nanoscale structures.

Figure 3.18 – A complementary color wheel produced by placing red, orange, yellow, green, blue, and violet bricks on top of black bricks.

Chapter Four - Structures and Their Construction at the Nanoscale

Devices that are of nanoscale dimensions and techniques used to prepare such devices will play an increasingly important role in technologies ranging from storage of data to imaging. LEGO® bricks are well suited to illustrate many of these developments. This chapter presents a sampling of the tools, materials, and devices that are helping us to image and manipulate matter at the nanoscale.

NOTE: LEGO® brick dimensions will often be described by numbers of pegs on their top surfaces. For example, a 2x4 brick is 2 pegs wide and 4 pegs long.

4.1 - Photolithography

Figure 4.1 contains a simple LEGO® representation of the process of photolithography. This complex process is essential to the manufacture of integrated circuits. Note that multiple steps and temporary structures are required to make one simple feature containing only two materials; fabrication of an entire integrated circuit can take hundreds of steps.

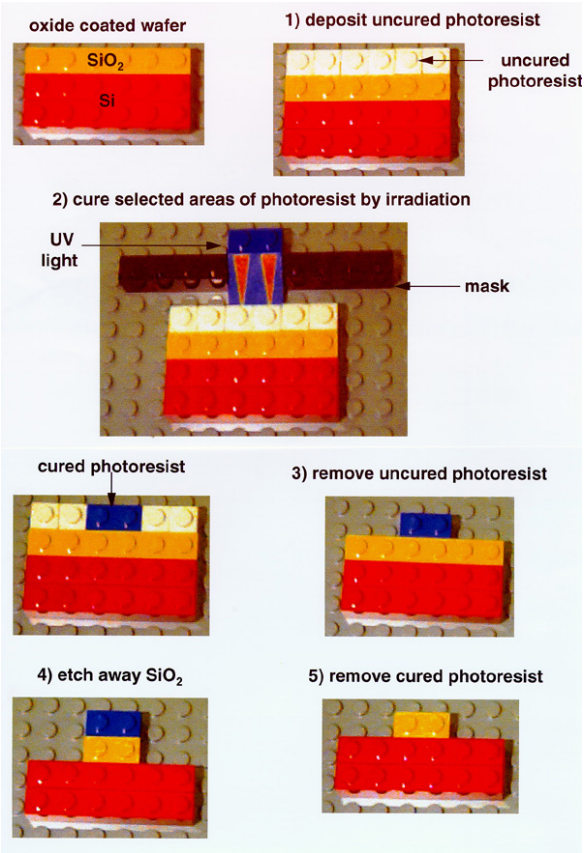


Figure 4.1 – A LEGO® model of photolithography.

Type of LEGO® brick	Number of LEGO® bricks
red 1x6 bricks	2
yellow 1x2 bricks	3
blue 1x2 brick	1
white 1x1 bricks	6
black 1x4 bricks	2
blue 2x3/25° roof tile	1

4.2 - Self-Assembly

How can you make a square pattern of LEGO® bricks like that shown?

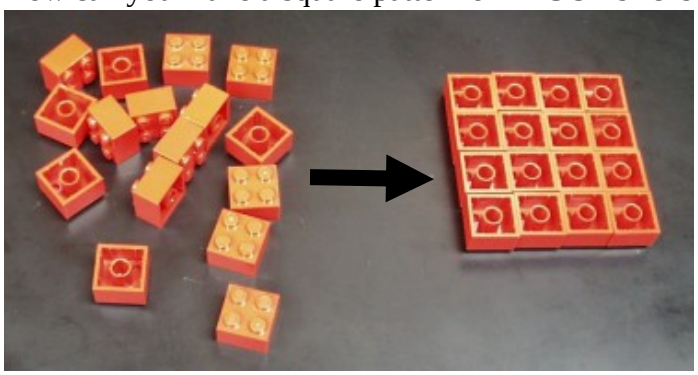


Figure 4.2 – A square array of 2x2 LEGO® bricks.

There are really two ways to do this. One is called the top-down approach, where a big structure is cut down in size until the desired shape is achieved. This is similar to carving a piece of wood down into a sculpture. For our LEGO® pattern we could take a big arrangement of bricks and remove the bricks we do not want until we get the pattern. However, this can be a bit wasteful and sometimes the patterns we want are still very difficult to build, especially very small patterns.

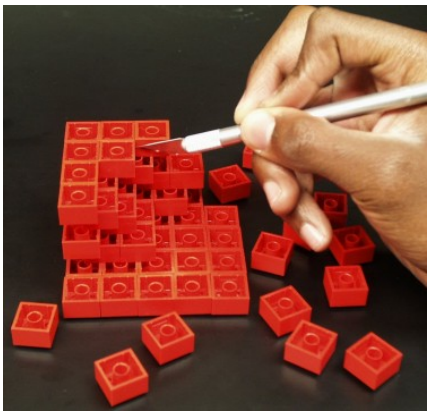


Figure 4.3 – Representation of the top-down approach for producing a structure from 2x2 bricks.

The other method is called the bottom-up approach, where a big structure is built up from smaller pieces. For objects you can see, feel, and pick up this method can be easy. The LEGO® pattern above is easily put together by hand. But what if the objects to be placed into a pattern were molecule-sized – in the realm of the nanoscale? To get an idea of the difficulty involved, try arranging grains of table salt into the same square pattern. You will probably find that your fingers are too big for the task. Try again using smaller manipulators such as toothpicks or tweezers to arrange the grains. This is still difficult. You will also find that it takes quite a while to make a sizable pattern.

Imagine then, how much more difficult and time-consuming a nanoscale pattern takes to make. It would be even better if the objects were designed so that they could arrange

themselves into the patterns. This type of fabrication is called "self-assembly". This can be demonstrated by placing several of the square LEGO® bricks peg side down on water in a big beaker. Do not flood the bricks with water. The bricks will interact with the surface tension of the water and each other to assemble into a square pattern. Gently tapping the beaker with your hand might help the structure to assemble.

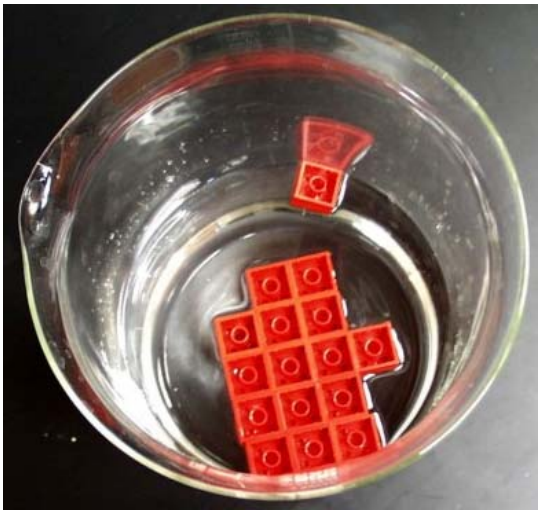


Figure 4.4 – Self-assembly of 2x2 bricks, an example of the bottom-up approach for producing a structure.

Many researchers are exploring self-assembly of small objects (even molecules) at the nanoscale level to produce very complex structures. This method may eventually be used to build computer circuits, an alternative to the photolithography technique described in Section 4.1.

4.3 - Linear Nanostructures

Researchers are constructing and studying nanoscale linear structures (sometimes called nanowires) on surfaces. To start, they must fabricate surfaces that have a series of atomic steps or terraces. This sort of surface can be easily modeled with LEGO® bricks, Figure 4.5.

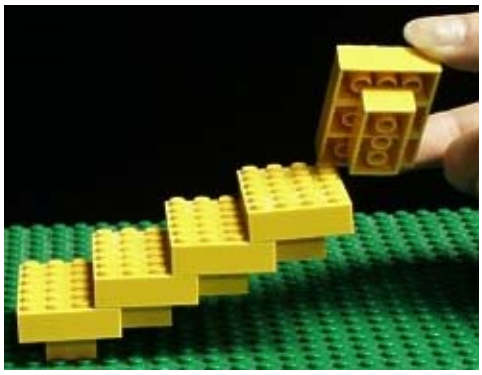


Figure 4.5 – Construction of a terraced LEGO® surface from 20 2x2 bricks.

When material is deposited on these surfaces, the deposited atoms sometimes migrate across the steps until they stop at the top of the step edges. A LEGO® model and scanning probe microscope image of this structure are shown in Figure 4.6.

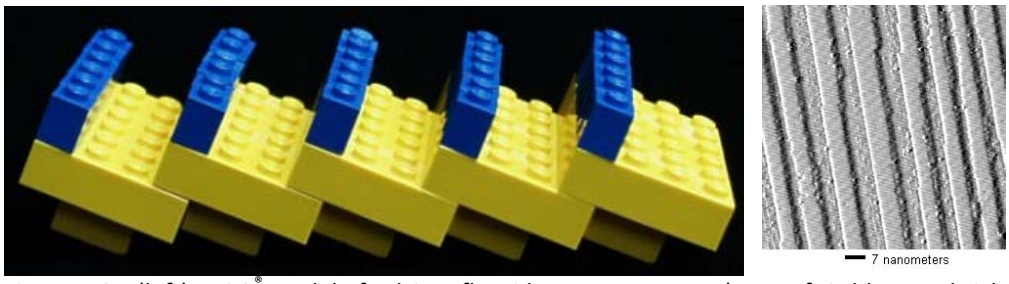


Figure 4.6 – (left) LEGO® model of calcium fluoride nanostructures (rows of six blue 1x1 bricks) on silicon terraces (yellow). (right) A scanning tunneling microscope image of such a nanostructure (top view). The dark stripes are shadows of the raised features.

The nanostructures can also form just below the step edges, as shown in the LEGO® model and the scanning tunneling microscope image in Figure 4.7.

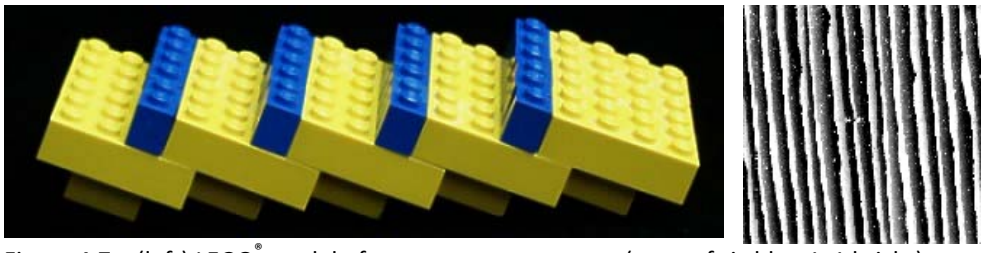


Figure 4.7 – (left) LEGO® model of copper nanostructures (rows of six blue 1x1 bricks) on molybdenum terraces (yellow). (right) A scanning tunneling microscope image (top view) of such a structure (copper is light, molybdenum is dark).

4.4 - Chain Reactions

Many chemical processes, such as those involved in the growth of some polymer molecules, involve chain reactions. A chain reaction involves many steps, which can be broken into three types:

1) Initiation - the starting step of the chain reaction.
2) Propagation - the repeating steps of the chain reaction. The end of each of propagation step can start another new propagation step.
3) Termination - the final step of the chain reaction, which stops the reaction process.

Chain reactions can be modeled with LEGO® bricks arranged to fall like dominoes. The falling units shown below can be made from 1x4 bricks attached to 2x4 bricks to make them more easily tipped. A chain reaction may be represented simply by a row of these bricks, Figure 4.8.

Figure 4.8 – A simple representation of a chain reaction using LEGO® bricks. Chain initiated from the right.

A chain reaction with a chain termination step may be represented by including a brick unit that will not tip over, Figure 4.9.

Figure 4.9 – A representation of a chain reaction with a chain termination step by a small tower of LEGO® bricks. Chain initiated from the right.

Branching chain reactions may also be represented by careful placement of the falling units, Figure 4.10.

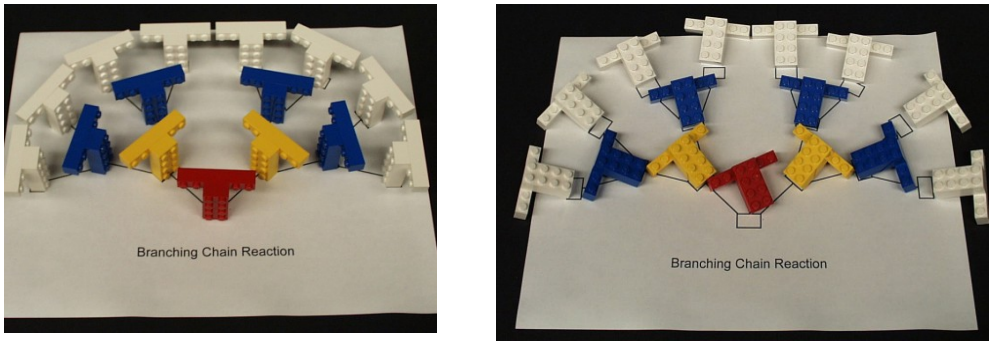


Figure 4.10 – A representation of a branching chain reaction using LEGO® bricks. Chain initiated from the center.

4.5 – Ferrofluid: Nanoscale Particles and Surfactants

Ferrofluid is composed of nanoscale magnetite (Fe_3O_4) particles suspended in solution. In order for the magnetite particles to remain in solution, they must be in the nanoscale size regime. This is accomplished by adding a layer of molecules called surfactants to the surface of each of the magnetite nanoparticles. The surfactant layers act as a bumpers to keep the magnetite particles from aggregating together and falling out of solution. This concept can be demonstrated by aggregation of magnetic LEGO® bricks.

The units in Figure 4.11, left, represent magnetite particles without a surfactant. Each unit (one is outlined with a black line) is made by placing a magnetic LEGO® brick over four 1x2 bricks. Two of these units have their magnetic north poles facing upward, and the other two units have their magnetic south poles facing upward. When these units are placed into a flat-bottomed container and shaken, they tend to aggregate together immediately to form large clusters comprised of many individual units. In a similar fashion, magnetite particles without protective surfactant layers magnetically aggregate. NOTE: The aggregation of these magnetic units can also be used as a demonstration of self-assembly, described in Section 4.2.

The units in Figure 4.11, right, represent magnetite particles surrounded by a surfactant. Each of these units is made by placing one of the units mentioned above on top of four 2x4 bricks. When these units are placed into a container and shaken, they do not aggregate as readily. In a similar fashion, magnetite particles with protective surfactant layers do not magnetically aggregate.

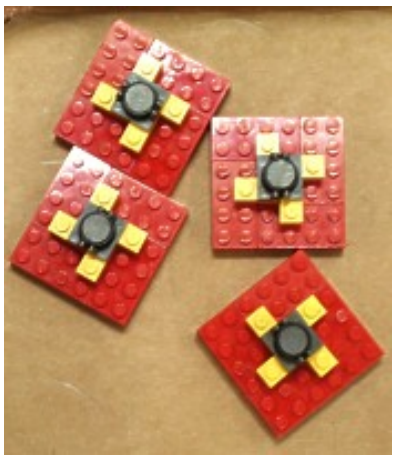


Figure 4.11 – (left) Aggregation of magnetic units, where each is a fixed LEGO® magnet on four 1x2 bricks. (right) Aggregation of magnetic units prevented by placing these units on bumper bricks (one 2x2 and four 2x4 bricks per unit).

4.6 – Photonic Crystals

Photonic crystals, like all other crystals, contain repeating structures. The scale of many of these repeating structures is the order of the wavelength of light. Light striking these crystals can be scattered and diffracted in a number of directions, depending on the exact structure of the crystal. These crystals are being studied for a number of applications in optics. Some of these crystals interact with light in a similar way that conventional semiconductors interact with electricity. It is possible that future computers will use photons rather than electrons as their basis of operation. Figure 4.12 shows an example of a photonic crystal.

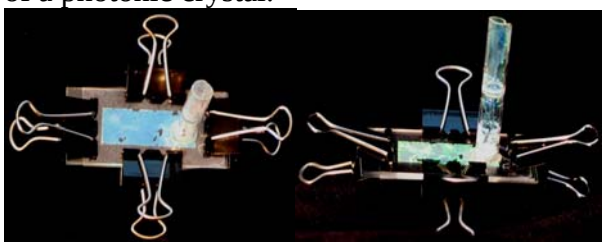


Figure 4.12 – This photonic crystal sandwiched between two glass slides is produced by assembly of polystyrene spheres only 356 nanometers in diameter into a face-centered cubic structure. The crystal can diffract white light into a range of different colors, and appears to be different colors in the two pictures because its viewing angle is different.

Some photonic crystals can be fabricated by self-assembly type methods (see Section 4.2). Often tiny spheres of various materials aggregate together as closely as possible,

resulting in face-centered cubic structures. A relatively simple model of the face-centered cubic structure and its unit cell is described in the Section 1.2 Appendix.

Other types of photonic crystals are made are fabricated by inserting material between the spheres of the existing crystal structures, and then dissolving the spheres themselves. The resulting structure, called an inverse opal structure, can be described as a solid containing a face-centered cubic arrangement of empty spheres. This fabrication method resembles photolithography (see Section 4.1) in that both techniques involve the use of temporary structures as forms or scaffolding to produce the desired structures. Models of a face-centered cubic unit cell of large spherical LEGO® clusters and its associated inverse opal structure are shown in Figure 4.13. The website associated with this book contains building instructions for these opal models, accessible from the page called LEGO® Molecular-Scale Models, http://mrsec.wisc.edu/Edetc/LEGO/index.html. Figure 4.14 shows an image of portions of a face-centered cubic structure of polymer spheres.

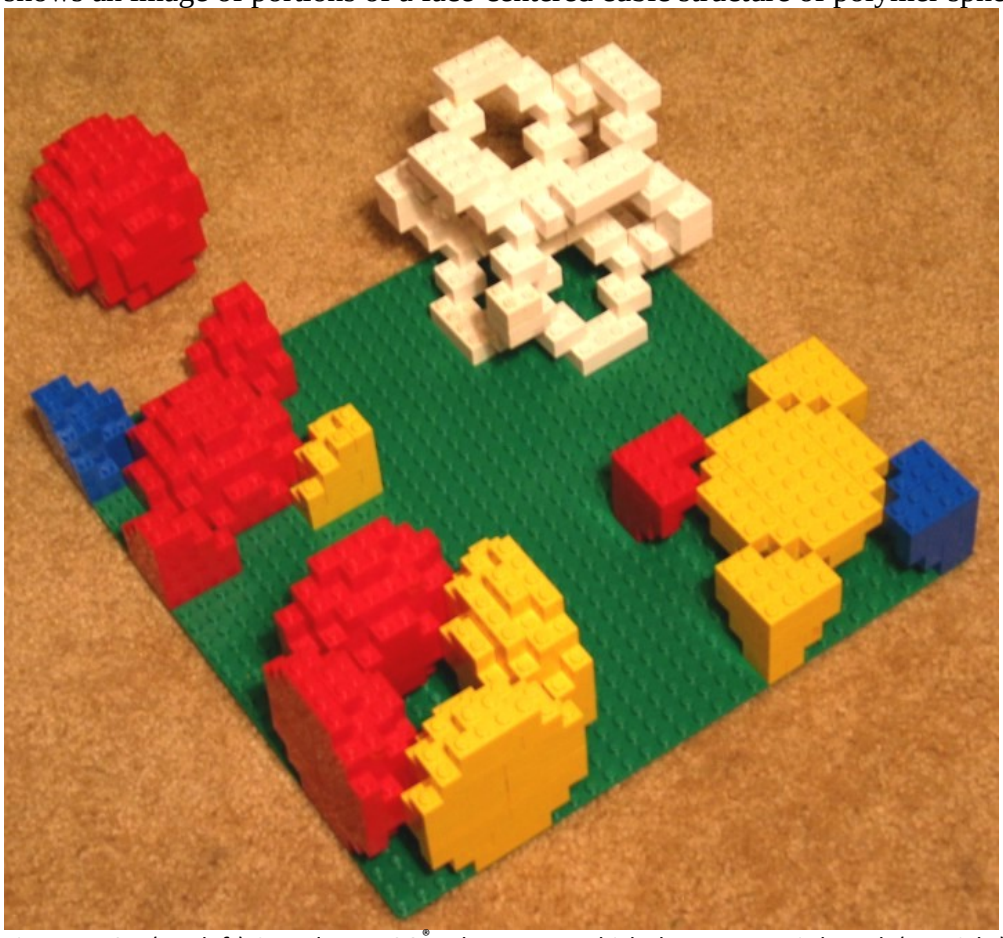


Figure 4.13 – (top left) Complete LEGO® sphere upon which the structure is based. (top right) Inverse opal based on the face-centered cubic unit cell. (bottom) Layers of the face-centered cubic unit cell. From left to right, the Z layers equaling 0, ½, and 1 are shown. The different colors represent the ABC sphere stacking layers of the structure.

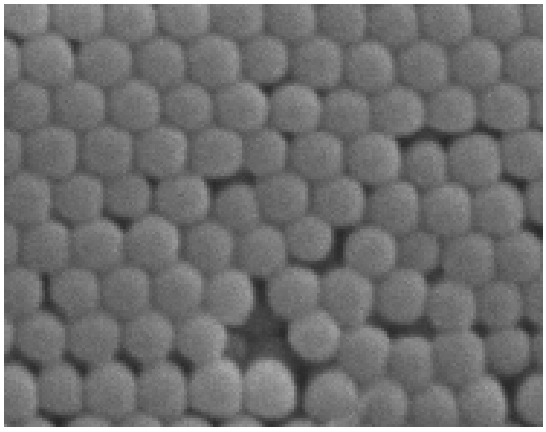


Figure 4.14 - A scanning electron microscope image of portions of a face-centered cubic structure of polystyrene spheres. The surface shown represents a single A, B, or C layer within the structure. The spheres are approximately 180 nanometers in diameter.

Photonic crystals that have a diamond-like structure (see Section 1.2 and its Appendix) have particularly interesting optical properties, but have proven very difficult to fabricate. Yet another type of photonic crystal of interest to researchers is comprised of crosswise stacked layers of linear structures. This structure has been referred to as a woodpile, and its model is depicted in Figure 4.15. This model can be thought of as being an arrangement of two-brick units such as the one shown near the bottom of the picture. Again, fabrication of this type of structure at a very small scale has been challenging.

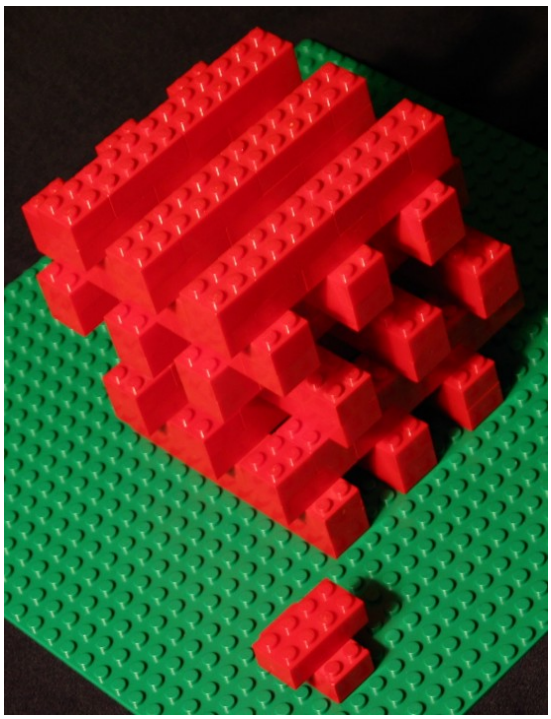


Figure 4.15 – A woodpile structure. Each of the 18 “logs” in this woodpile model is made of five2x4 and two 2x2 bricks.

4.7 – Dialysis

Dialysis has long been used purify blood and other solutions containing biomolecules, but it has also been used to purify non-biological nanostructures. The most important component of the dialysis technique is a porous membrane. The pores only allow small molecules like water or small ions to pass through. Larger species, such as nanoparticles, are too large to pass through the membrane. Figure 4.16 shows a brown-colored suspension of carbon nanoparticles in salty water. The salt must be removed from the nanoparticles, so the suspension is placed in a tubular dialysis membrane, which is in turn placed in pure water. The water and salt ions can flow in and out of the small pores in the membrane, so the ions will migrate from high salt concentration inside the tube to low concentration outside the tube. The carbon nanoparticles are too large to pass through the pores in the membrane and are separated from the salt ions.

Figure 4.16 – A brown suspension of carbon nanoparticles in a tubular dialysis membrane. The nanoparticles cannot pass through the pores of the membrane, but water molecules can pass.

This dialysis technique can be modeled with LEGO® bricks, as shown in Figure 4.17. A divided box is built from simple bricks and then a few additional loose bricks are placed in the box. When the box is shaken sideways, the loose bricks will move around as a model of molecules and nanoparticles in liquid. The divider has small channels that will allow small loose bricks (molecules) to pass between sides of the box, but not large loose bricks (nanoparticles).

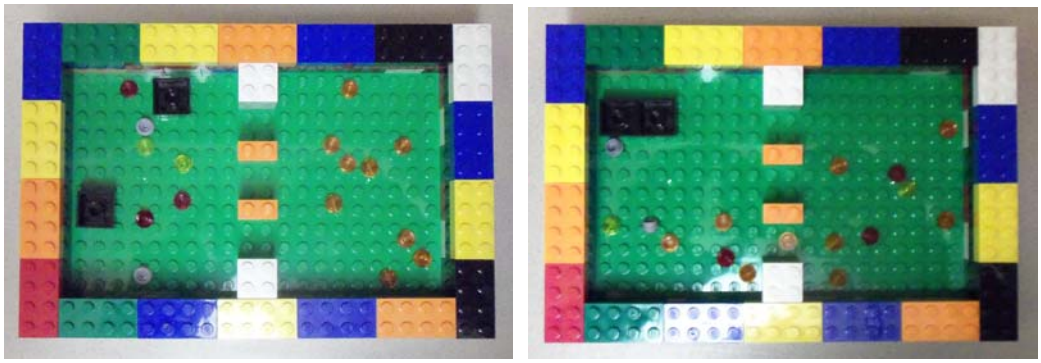


Figure 4.17 – (left) LEGO® brick box with walls and a divider that contains channels that are 2 pegs wide. The floor of the box is 16x24 pegs, and the walls and divider are comprised of 3 layers, with each layer containing 18 2x4bricks, two 2x2 bricks, and two 1x2 bricks. Initially, the left side contains various colors of one-peg small bricks and a couple of larger 2x2 bricks. The right side contains only orange one-peg small bricks. (right) After the box is shaken sideways, the one-peg bricks have migrated between the sides of the box through the channels in the divider. The 2x2 bricks are too large to pass through the channels.

References/Additional Reading

Campbell, D. J.; Bailey, R. A. "Density Tricks with LEGO® Bricks." *Chem13 News,* **Feb, 2003**, 4-5.

Campbell, D. J.; Beckman, K. J.; Calderon, C. E.; Doolan, P. W.; Ottosen, R. M.; Ellis, A. B.; Lisensky, G. C. "Replication and Compression of Bulk and Surface Structures with Polydimethylsiloxane Elastomer." *J. Chem. Educ.,* **1999,** *76,* 537.

Campbell, D. J.; Freidinger, E. R.; Hastings, J. M.; Querns, M. K. "Spontaneous Assembly of LEGO®s." *Chem13 News,* **Sep, 2001**, 8-9.

Campbell, D. J.; Korte, K. E.; Xia, Y. "Fabrication and Analysis of Photonic Crystals"*J. Chem. Educ.,* **2007,** *84,*1824-1826.

Campbell, D. J.; Kuech, T. F.; Lisensky, G. C.; Lorenz, J. K.; Whittingham, M. S.; Ellis, A. B. "The Computer as a Materials Science Benchmark." *J. Chem. Educ.,* **1998,** *75,* 297.

Campbell, D. J.; Olson, J. A.; Calderon, C. E.; Doolan, P. W.; Mengelt, E. A.; Ellis, A. B.; Lisensky, G. C. "Chemistry with Refrigerator Magnets: From Modeling of Nanoscale Characterization to Composite Fabrication." *J. Chem. Educ.,* **1999,** *76,* 1205-1211.

Campbell, D. J.; Querns, M. K. "Illustrating Poisson's Ratios with Paper Cutouts." *J. Chem. Educ.,* **2002,** *79,* 76.

Campbell, D. J.; Xia, Y. "Powder Diffraction Simulated by a Polycrystalline Film of Spherical Colloids" *J. Chem. Educ.,* **2006,** *83,* 1638-1642.

Ellis, A. B.; Geselbracht, M. J.; Johnson, B. J.; Lisensky; G. C.; Robinson, W. R. *Teaching General Chemistry: A Materials Science Companion;* American Chemical Society: Washington, DC, 1993.

Ellis, A. B.; Kuech, T. F.; Lisensky, G. C.; Campbell, D. J.; Condren, S. M.; Nordell, K. J. "Making the Nanoworld Comprehensible: Instructional Materials for Schools and Outreach." *J. Nanoparticle. Res.,* **1999,** *1,* 147.

Garvey, C. J.; Hammer, D. M.; Prasertchoung, S.; Gomar-Nadal, E.; Hines, D. R.; Miller, J. D.; Campbell, D. J. "Demonstrating Photolithography with LEGO® Bricks." *The Chemical Educator,* **2008,** *13,* 348-350.

Lorenz, J. K.; Olson, J. A.; Campbell, D. J.; Lisensky, G. C.; Ellis, A. B. "A Refrigerator Magnet Analogy to Scanning-Probe Microscopy." *J. Chem. Educ.,* **1997,** *74,* 1032.

Santamaria, F. G. Ph.D. Thesis, Universidad Autonoma de Madrid, Madrid, Spain, 2003.

Materials Research Science and Engineering Center for Nanostructured Materials and Interfaces.
http://mrsec.wisc.edu/Edetc/

ICE Solid State Model Kit.
http://ice.chem.wisc.edu/Catalog/SciKits.html#Anchor-Solid-31140

Movies of the following models can be seen at:
http://mrsec.wisc.edu/Edetc/cineplex/LEGO/index.html

- negative Poisson's lattice
- giant magnetoresistance structure
- charge-coupled device (different model than shown in this booklet)
- magnetic force microscope (different model than shown in this booklet)

Assessment Form

Please mail the completed form to:

Dr. Dean Campbell
Bradley University
Chemistry Department
Peoria, IL 61625
campbell@bradley.edu

---

1. Who attempted to build the models?
   Gender: ___ female ___ male

   Occupation: ___ student ___ teacher ___other:_____

   Age range:___ < 10 ___ 10-14 ___15-20 ___ 20-30 ___>30

   Experience with LEGO® bricks: ___ beginner ___ intermediate ___ advanced

2. Which models were built (or attempted)?

Model	**Attempted?Built?**	**Difficulty rating?(1 easy; 5 very hard)**
Solid/liquid/gas		
2-dimensional unit cells		
3-dimensional unit cells		
Solid solutions		
Atomic force microscope		
Charge-coupled devices		
Spectrophotometer		
Polymer cross-linking		
Poisson's ratio lattice		
Silicates		
Linear nanostructures		
Magnetoresistance structures		

3. What difficulties were encountered with the building instructions in the book?

4. Did the text clearly explain the link between the science concepts and the LEGO® models that you built?

4. Please place X's in the boxes below to indicate which topics are suitable for which education levels.

Concept	**Grade School**	**Middle School/ Junior High**	**High School**	**College (introductory)**	**College (advanced)**
Solid/liquid/gas					
2-dimensional unit cells					
3-dimensional unit cells					
Solid solutions					
Atomic force microscopy					
Charge-coupled devices					
Spectrophotometers					
Polymer cross-linking					
Poisson's ratio					
Silicates					
Linear nanostructures					
Magnetoresistance					

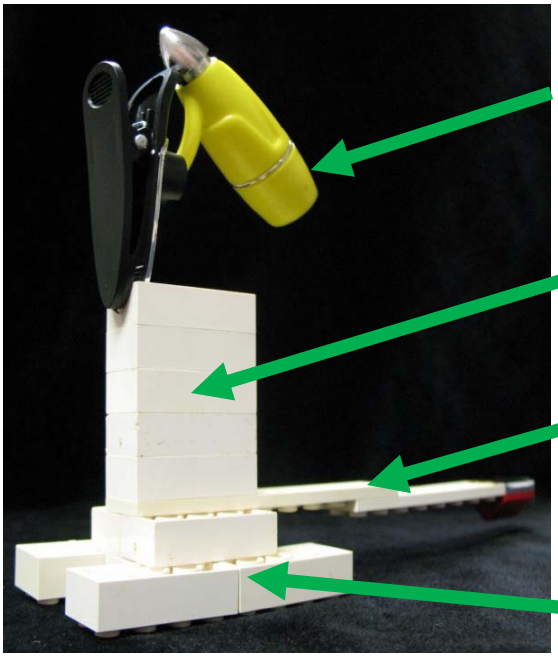
5. What topics do you think should be added to the booklet?

Scanning Probe Microscopes

<u>This atomic force microscope model requires:</u>
12 2x4 bricks light source (e.g. an LED book light)
2 2x10 plates reflective surface (metallized Mylar)
a plate and a brick or two are used for the substrate

Many versions of this model have been made with more bricks, automated substrate motion , lasers instead of LED light sources, and glass rather than plastic mirrors. This simple model requires the fewest bricks and is relatively inexpensive. Additional bricks and tape or rubber bands might be required to support a different light source.

Note that the brick pegs point downward in this model.

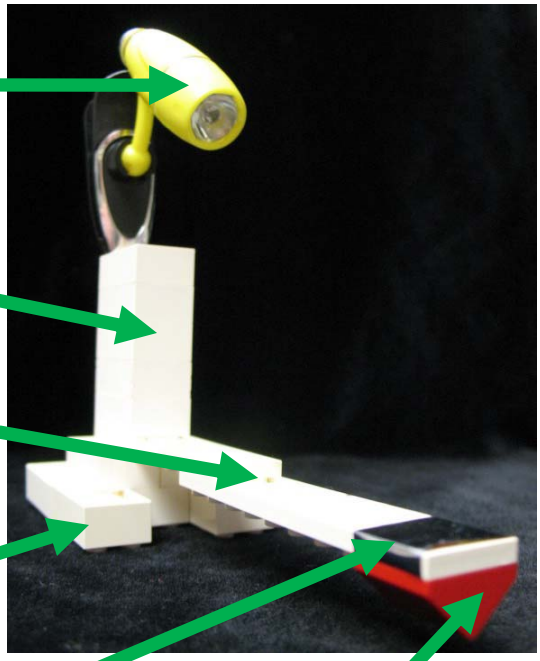


light points at mirror

five 2x4 brick tower

cantilever two 2x10 peg plates

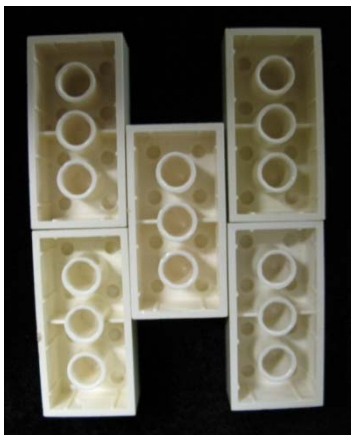
base



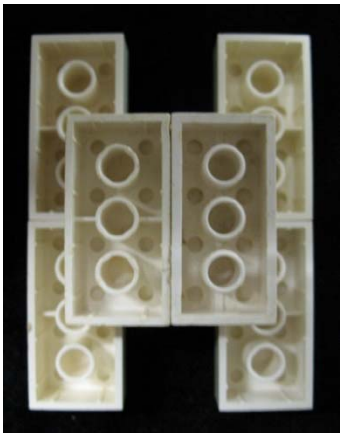
metallized Mylar strip

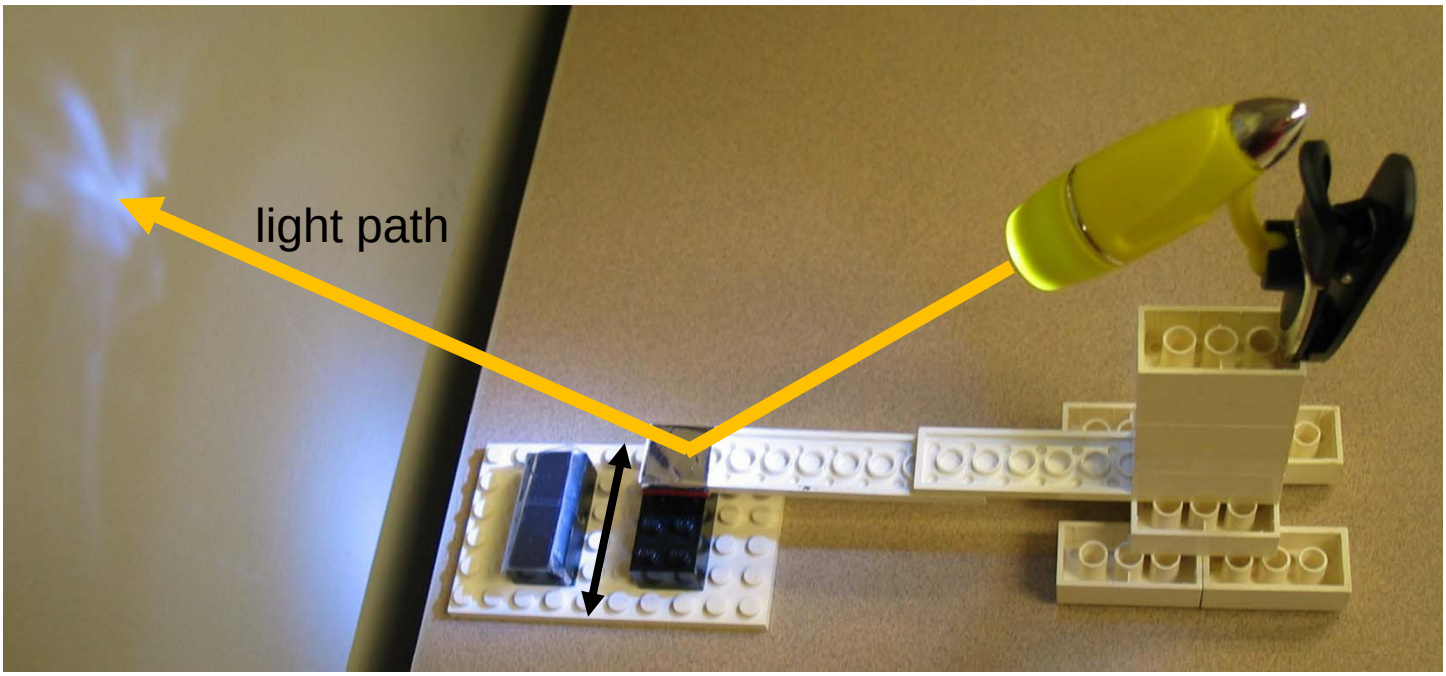
probe (2x 2 ridged tile)

Base Layer One: five 2x4 bricks



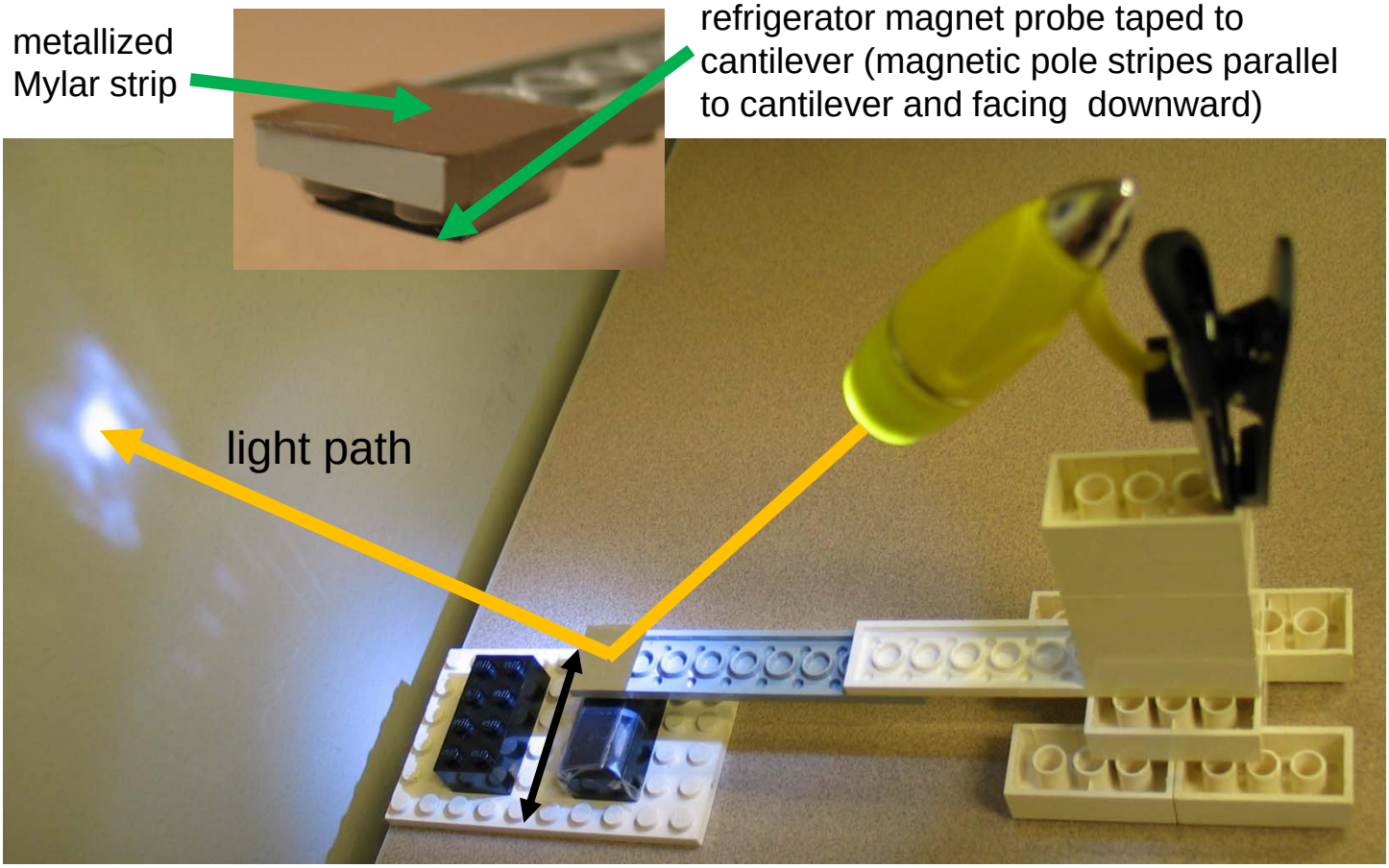
Base Layer Two: two 2x4 bricks





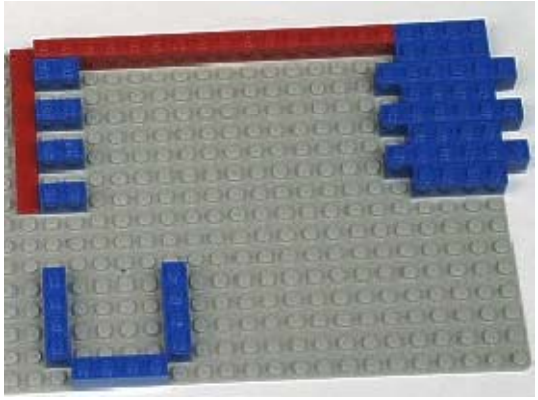
Substrate is a regular brick on a flat brick. Substrate motion is perpendicular to light path.

Modifications for Magnetic Force Microscope

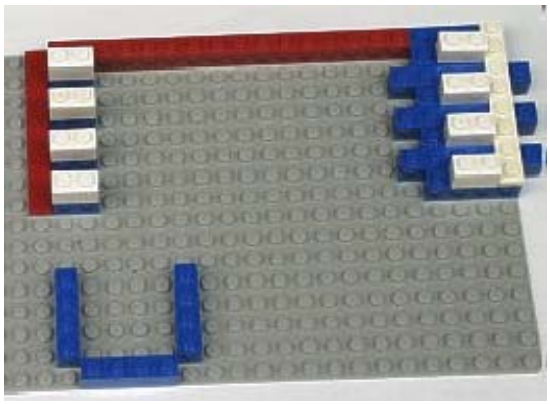


Substrate is a refrigerator magnet taped to a regular brick on a flat brick. Substrate motion is perpendicular to magnetic pole stripes in the substrate and the cantilever as well as the light path.

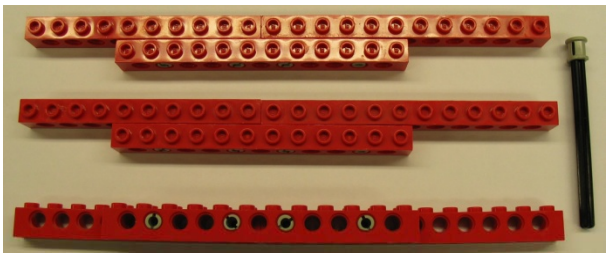
Charge-Coupled Device



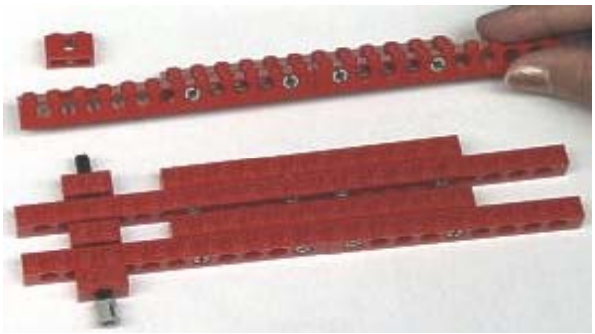
Layer 1

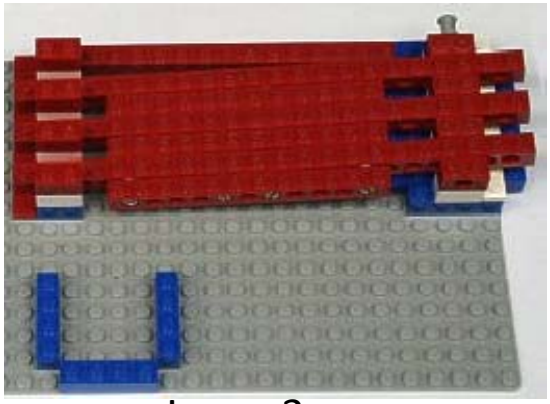


Layer 2

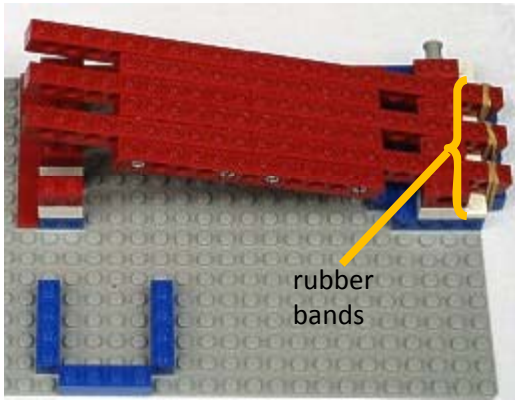


Details of axle/lever assembly

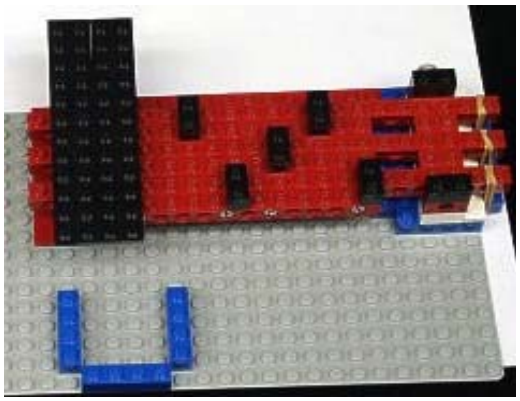




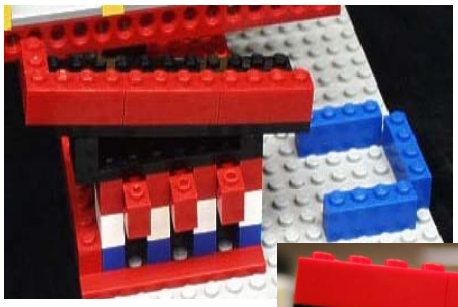
Layer 3



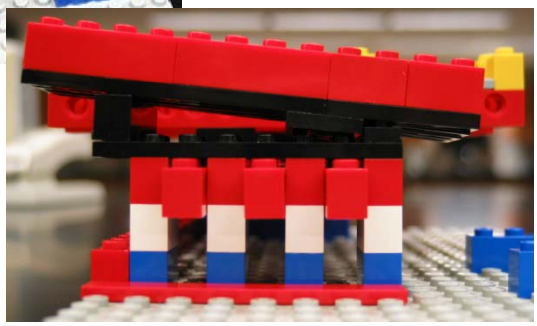
Detail of rubber band placement

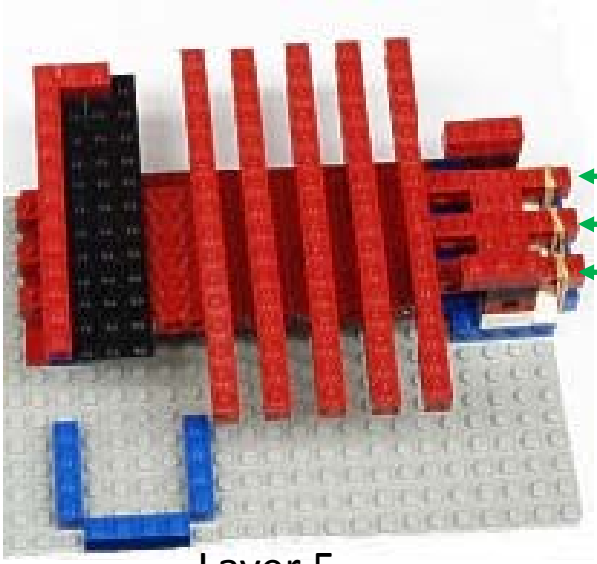


Layer 4

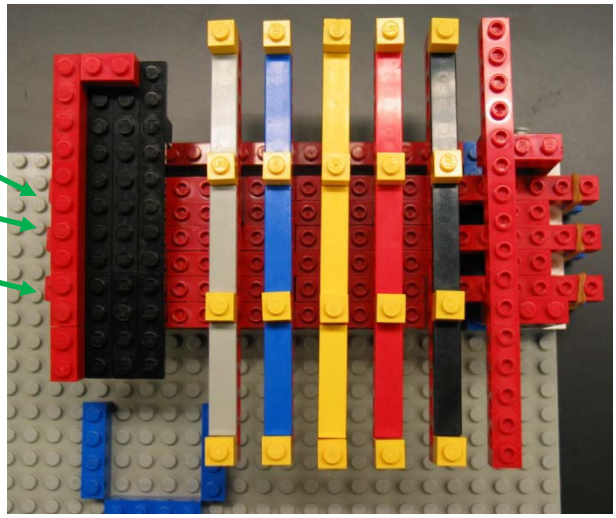


Details of ramp assembly

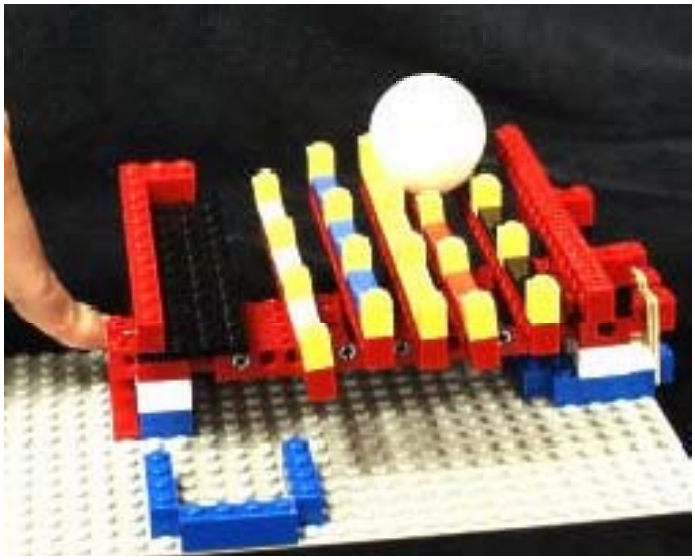




Layer 5



Layer 6



A table tennis ball (representing an electron) can be placed anywhere on the platform. The different smooth sites represent electrodes in a CCD array. Slowly press and slowly release the levers in sequence (this represents changing the voltages on the electrodes) to move the ball to the ramp. The ramp represents the readout register of the CCD.

Brick Count

Blue

- 3 1x6 bricks
- 8 1x4 bricks
- 4 1x2 bricks
- 3 1x4 flat plates

Red

- 9 1x4 brick
- 1 1x8 flat plate
- 6 1x10 Technic bricks
- 4 1x2 Technic bricks
- 3 1x12 Technic bricks
- 8 1x2 bricks
- 2 1x8 plates
- 1 1x4 plate
- 2 1x3 bricks
- 1 1x12 Technic bricks
- 1 1x16 Technic bricks
- 3 1x4 flat plates

White

- 8 1x2 bricks
- 1 1x8 plate

Yellow

- 20 1x1 bricks
- 3 1x4 flat plates

Black

- 6 1x2 bricks
- 3 1x4 flat plates
- 4 1x12 plates

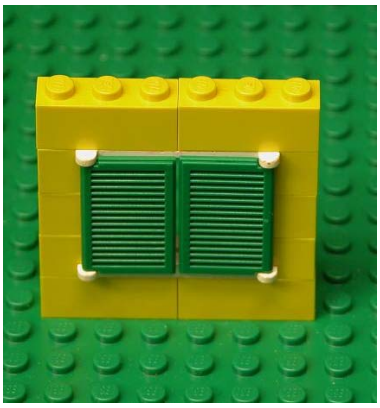
Gray

- 1 16x32 base plate
- 3 1x4 flat plate

NXT Photometer

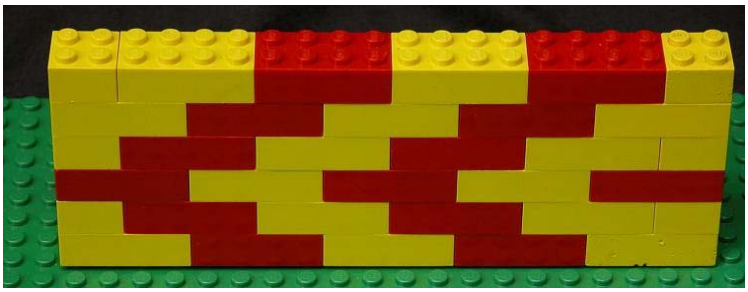
Sensor & Mount Parts:
2 1x2 Technic bricks,
1 cross axle #6,
4 1/2 bush pieces
1 light sensor

Sensor & Mount Assembled

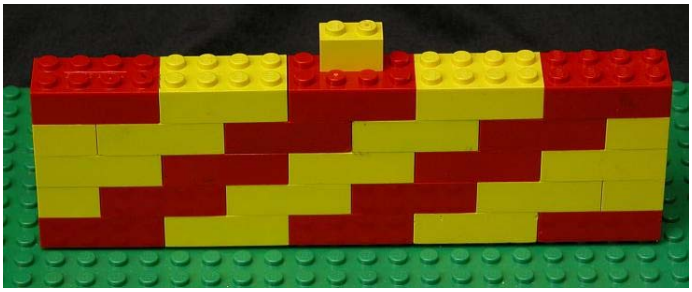


Light Shutter Wall:
4 1x3 bricks
6 1x2 bricks
1 frame 1x4x3
2 shutters 1x2x3

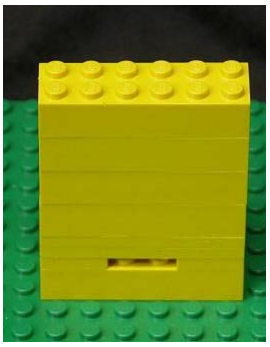
NXT control system required



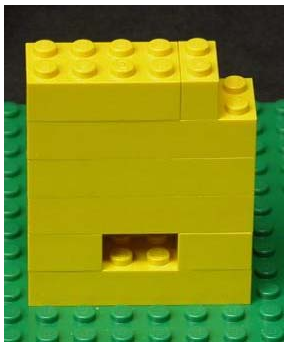
Back Wall: 27 2x4 bricks, 6 2x2 bricks



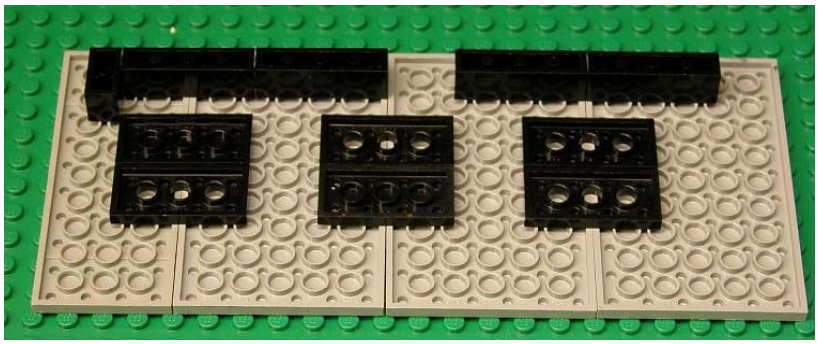
Front Wall: 23 2x4 bricks, 4 2x2 bricks, 1 1x2 brick



Sensor Cord Wall:
5 2x6 bricks
1 2x6 plate
2 2x2 plates



Light Entry Wall:
4 2x6 bricks
2 2x2 bricks
1 2x4 brick
1 1x2 brick

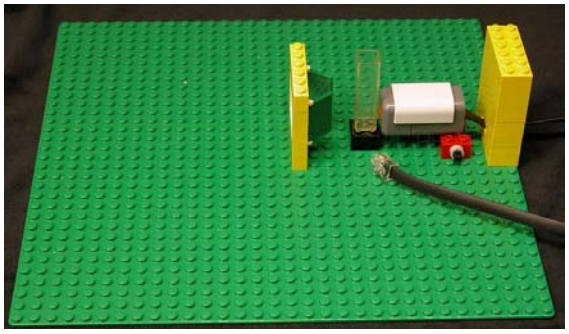


Lid: 1 4x10 plate, 3 6x10 plates, 6 2x4 plates,
4 2x4 bricks, 1 1x2 brick

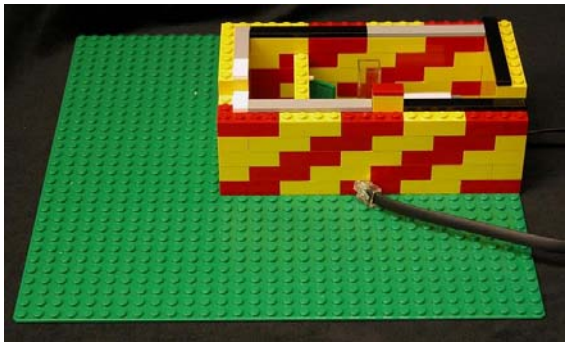
Plastic cuvette
glued to 2x2 brick

White light source
such as flashlight
also required

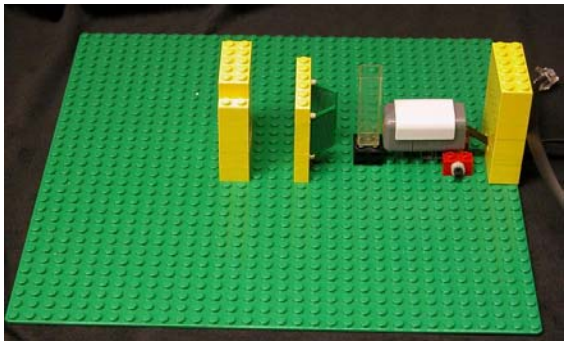
Building Instructions



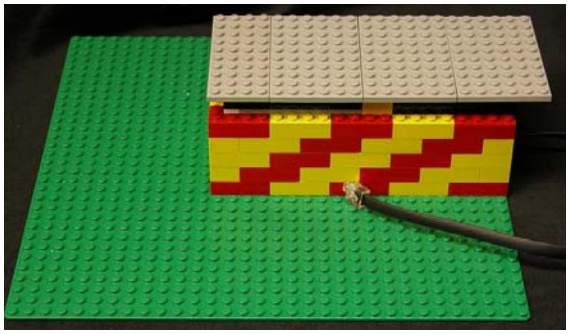
Placement of light shutter, cuvette, sensor, and right wall with cord running through.



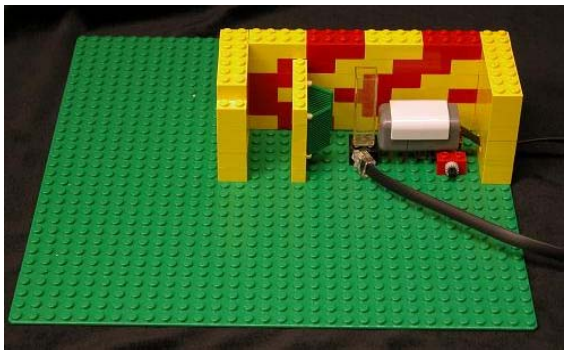
Flat tiles along the tops of the walls allow lid to be easily removed and replaced.



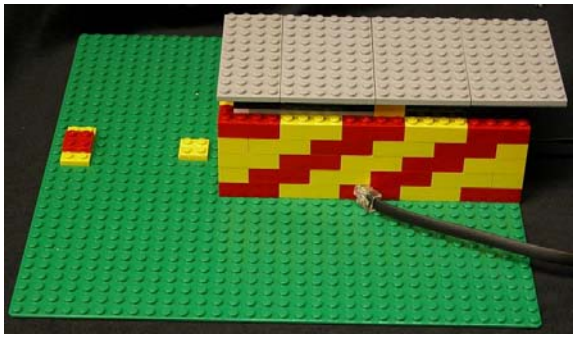
Placement of left wall



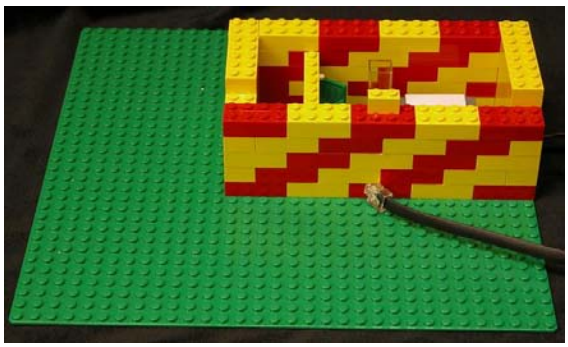
Placement of the lid



Placement of the back wall



Placement of light source mount



Placement of front wall

Finished model

Note: light mounts may vary from flashlight to flashlight.

Note: a dark cloth can be used in place of the walls

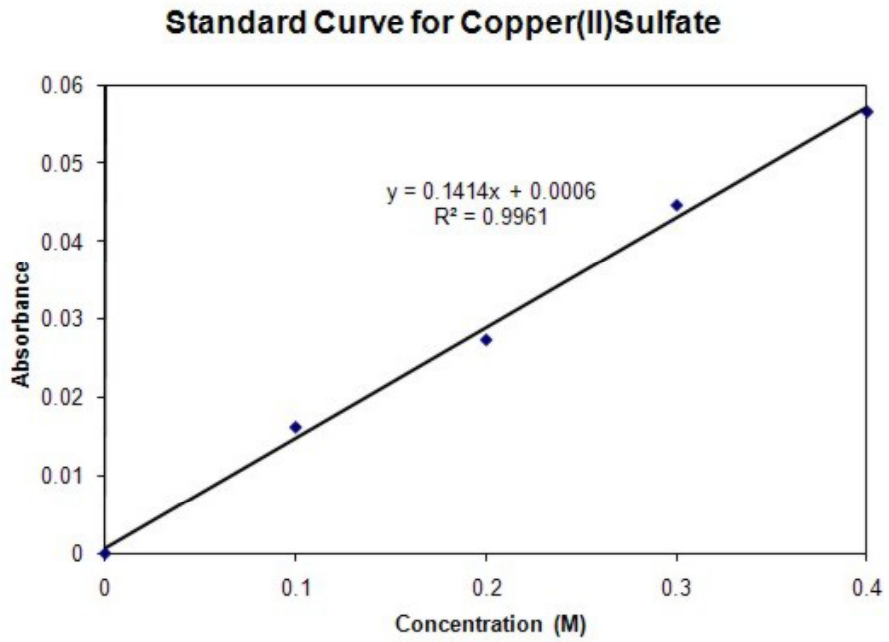
Producing a calibration curve

•To produce a calibration curve, measure the absorbance of deionized water and least three solution samples with differing concentrations. The solutions are placed in the cuvette for measurement. It is best to start with the most dilute solution and then move to increasing solution concentrations.

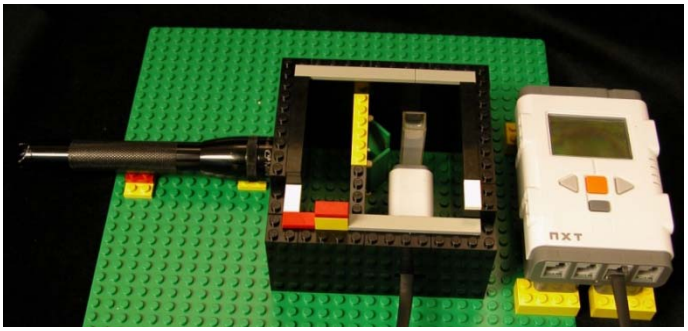
•To start taking measurements:

- •Turn on the NXT and make sure the light sensor is plugged in.
- •On the NXT click on “view”, click on “light sensor”, and then click on the port option that corresponds to port connected to the light sensor.
- •The light intensity reading are displayed directly on the NXT system as a % (not to be confused with % transmission). If the reading exceeds “99%”, the light intensity reaching the detector is too high and must be decreased by closing the shutter. The shutter position should stay constant for a particular set of measurements.

•The intensity readings from the NXT can be placed in a spreadsheet, as well as the solution concentrations. To convert the intensity readings to transmittance, divide the intensity reading of each solution by the intensity reading of deionized water. This fraction can be multiplied by 100% to get % transmittance. For absorbance, take the –log (fractional transmittance). Graphing absorbance as a function of concentration will produce a calibration curve. The absorbance of an unknown sample can be compared the calibration curve to find its concentration.



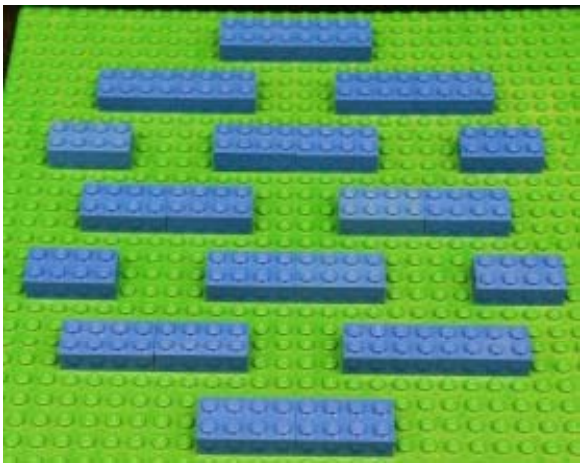
Photometer in a scattering geometry



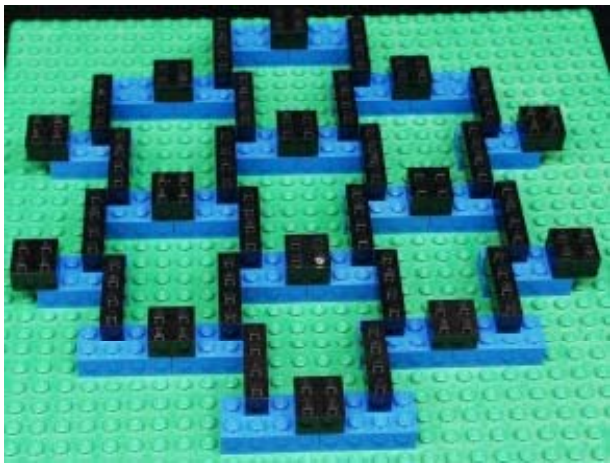
Poisson's Lattice

<u>This model requires:</u>
24 blue 2x4 bricks
14 black 2x2 bricks
20 black 1x4 brick
24 red 2x4 bricks
10 yellow 2x4 bricks

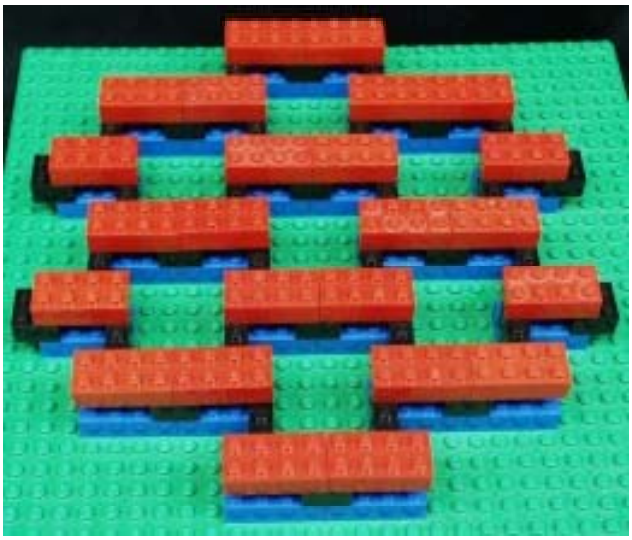
It might be easier to build the lattice over a flat LEGO® baseboard and then peel the baseboard away from the final lattice.



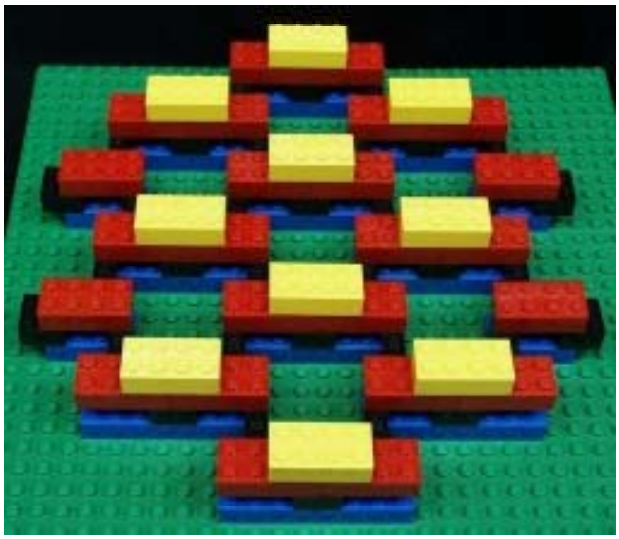
Layer 1



Layer 2



Layer 3



Layer 4

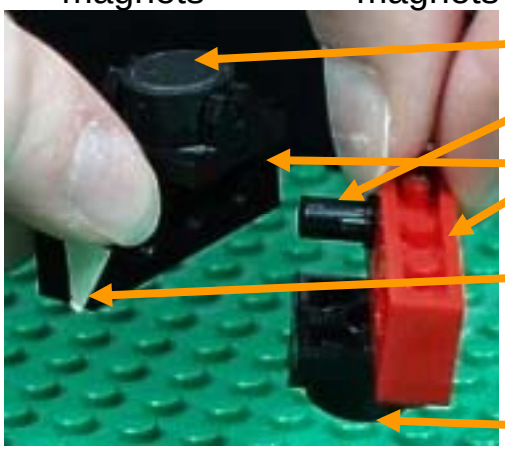
Giant Magnetoresistance (GMR) Structure

Magnetic Unit Construction

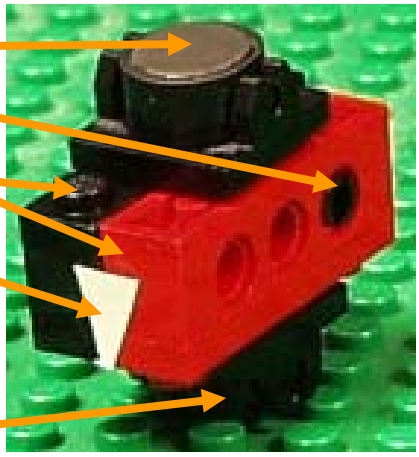
This structure requires 8 face-poled LEGO magnets, 4 in each orientation. Making a stack as shown helps to determine the orientation of each magnet. NOTE: It is not necessary to know the absolute orientation of each magnet, just that some are oriented one way and the others are oriented the other way. The “north” and “south” designations here are arbitrary.

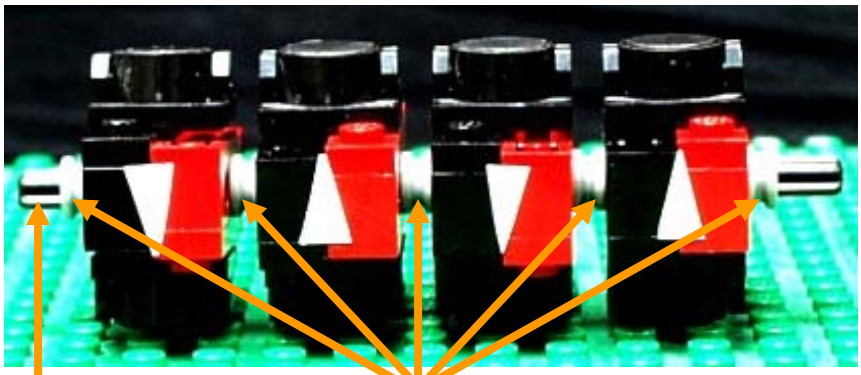
“north”-topped magnets “south”-topped magnets

Also required: light source, strong magnet, tape
Technic bricks: 4 red 1x16, 4 blue 1x4,
4 red 1x4, 4 black 1x4, 2 gray 1x2
Bricks: red 2x4, 2 red 1x2
Plates: 4 red 1x4, 4 black 1x4
8 connector pegs w.friction, cross axle 14M
five1/2 bush pieces



“south”-topped magnet
connector peg w.friction
1x4 Technic bricks
tape arrows to show magnetic field orientation (MUST be the same orientation for each unit)
“north”-topped magnet

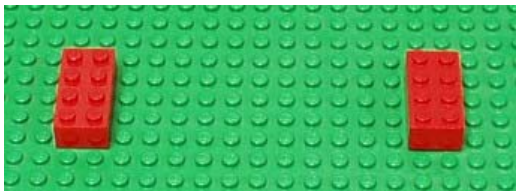




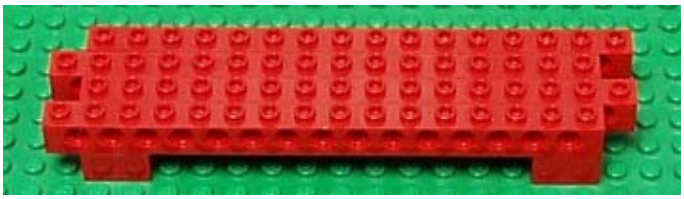
cross axle 14M five1/2 bush pieces

Note that the units spontaneously align themselves in an antiparallel arrangement.

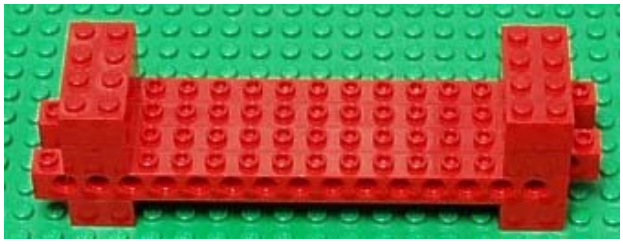
Platform Construction



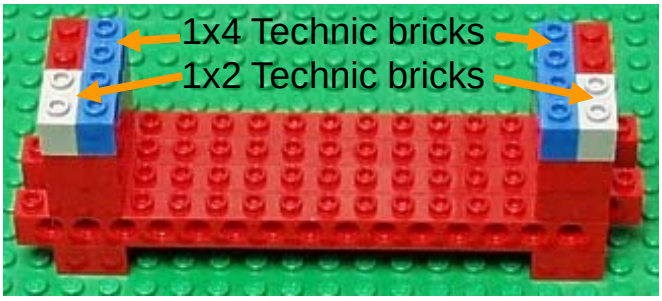
Layer 1



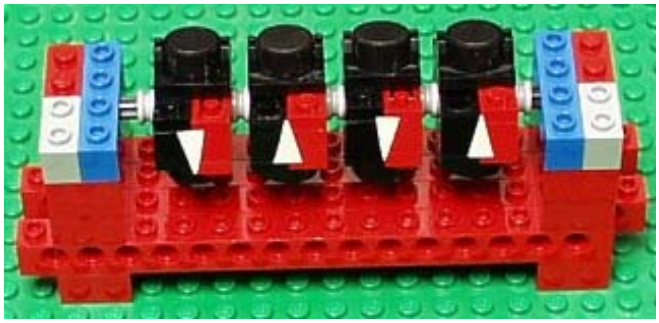
Layer 2



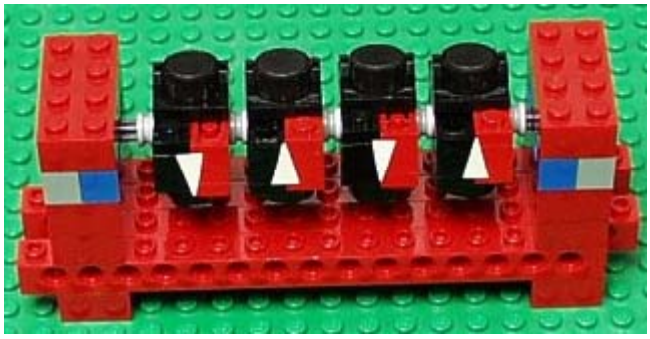
Layers 3 & 4



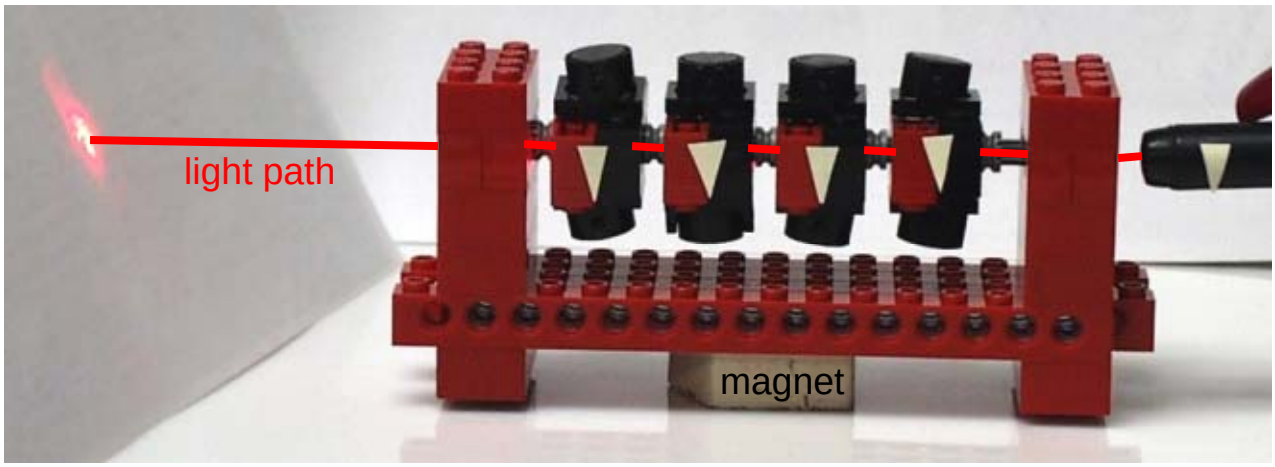
Layer 5



Insert axle with units into Layer 5



Layer 6



When a very strong magnet in placed under the platform, the magnetic units will all align in the same direction, allowing light to pass through the holes in the LEGO beams.