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?

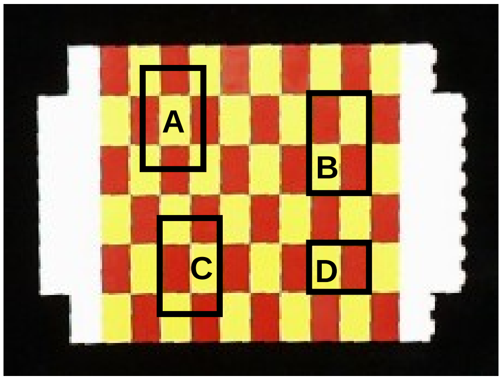

Figure 1.2 - Trial unit cells. A, B, C, and D are parallelograms. Which of these can be shifted along each of its edges by the length of the edge to create a replica of its contents?

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.

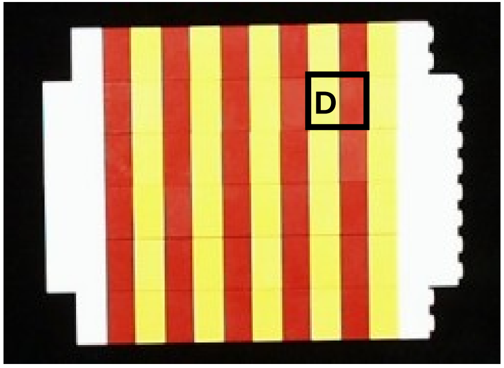

Figure 1.3 - The pattern formed by replicating D (black rectangle). Since D is not a unit cell of Figure 1.2, the generated pattern does not match Figure 1.2.

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.

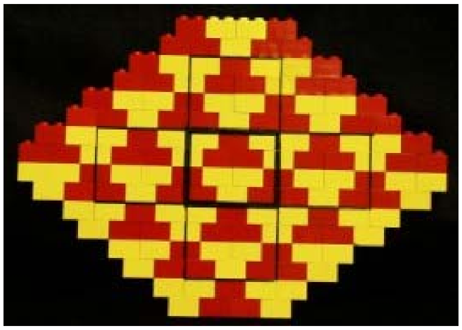

Figure 1.4 - Two-color 1x2 brick wall formed. A unit cell is outlined in black in the center and has been shifted in all four directions to show that all of the shifts yield parallelograms with identical contents to the original parallelogram.

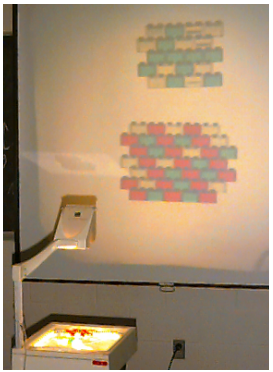

Figure 1.5 - With translucent LEGO® bricks, the brick walls can be shown to large groups using an overhead projector.

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.

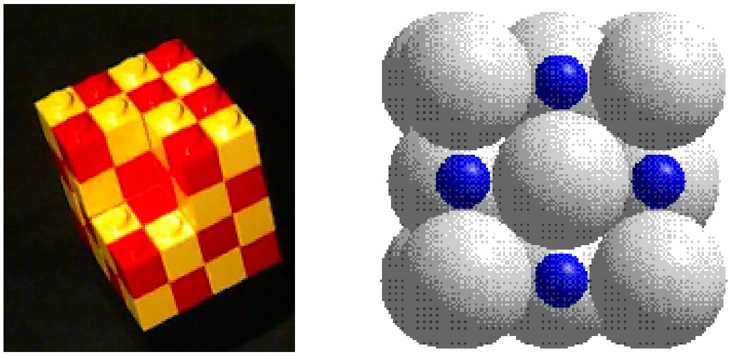

Figure 1.6 - (left) The sodium chloride structure as depicted with 1x1 LEGO® bricks. (right) The sodium chloride structure shown with small blue spheres representing sodium ions and the large white spheres representing chloride ions.

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.

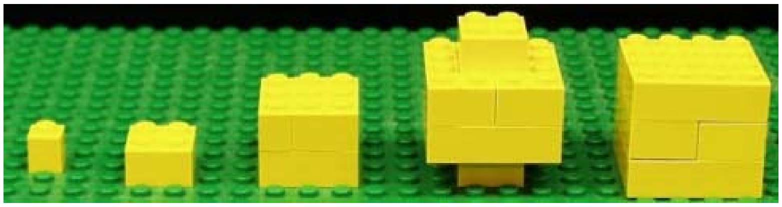

Figure 1.7 - Different possible arrangements of bricks to represent atoms (left to right): 1x1 brick; 2x2 brick; cluster of two 1x3 bricks and two 2x3 bricks; cluster of two 2x2 bricks and four 2x4 bricks; cluster of six 2x4 bricks.

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.

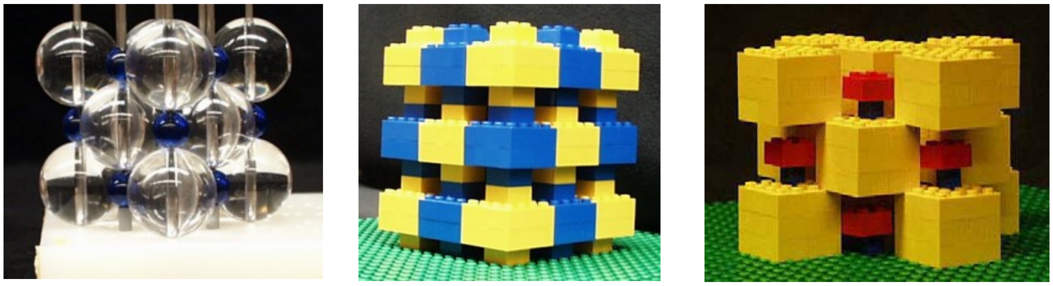

Figure 1.8 - Models of the sodium chloride structure, all featuring 13 sodium ions and 14 chloride ions. (left) Model made with the Institute for Chemical Education Solid State Model Kit - the small blue spheres represent the sodium ions and the large colorless spheres represent the chloride ions. (middle) 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.

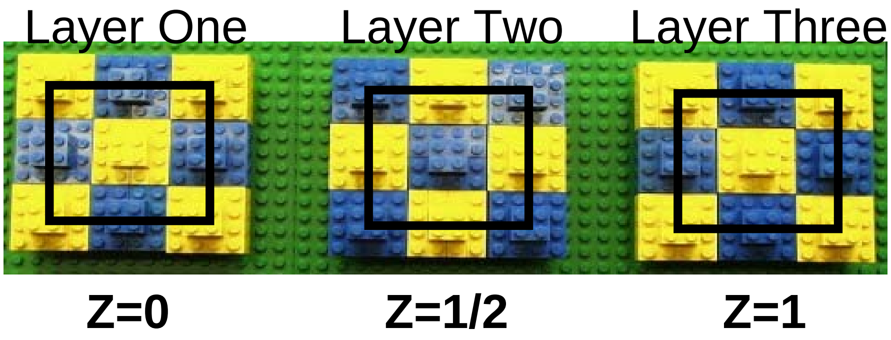

Figure 1.9 - The layer sequence of the sodium chloride unit cell depicted in Figure 1.8 (middle picture). Each cluster of two 2x2 bricks and four 2x4 bricks represents an ion. The black squares drawn over the pictures depict actual unit cell boundaries; the corners of the cubic unit cell lie at the centers 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.

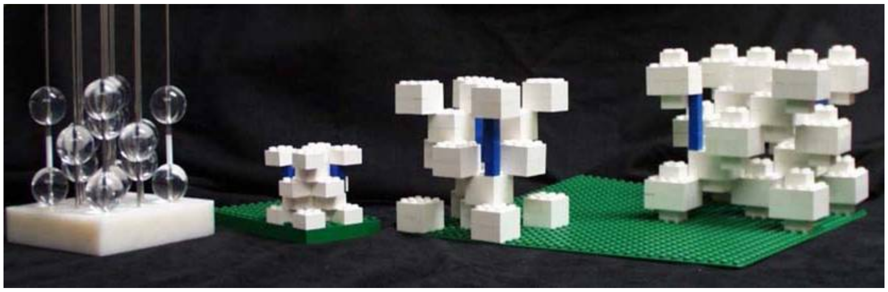

Figure 1.10 - Several models of the diamond unit cell, each comprised of 18 "atoms". The model at the left is made with the Institute for Chemical Education Solid State Model Kit. The LEGO® brick models are made with: 2x2 bricks; clusters of two 1x3 bricks and two 2x3 bricks; and clusters of two 2x2 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.

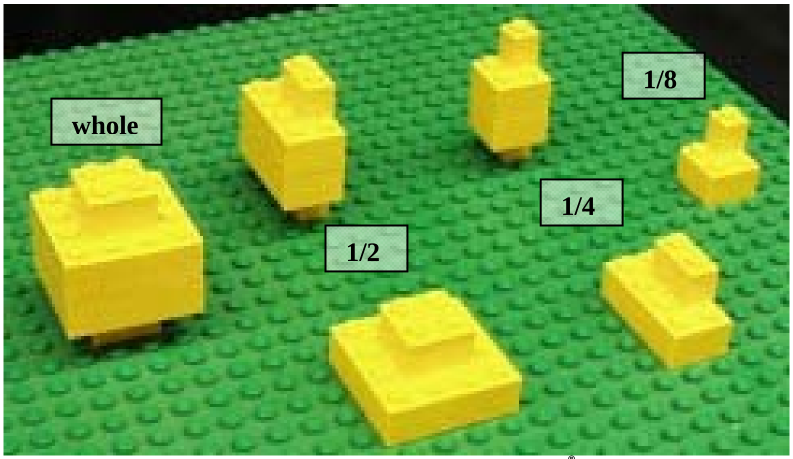

Figure 1.11 - Modeling fractions of atoms with LEGO® bricks. From left to right:
whole atom as a cluster of two 2x2 bricks and four 2x4 bricks,
1/2 atom as a cluster of two 1x2 bricks and two 2x4 bricks,
1/2 atom as a cluster of one 2x2 bricks and two 2x4 bricks,
1/4 atom as a cluster of two 1x1 bricks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

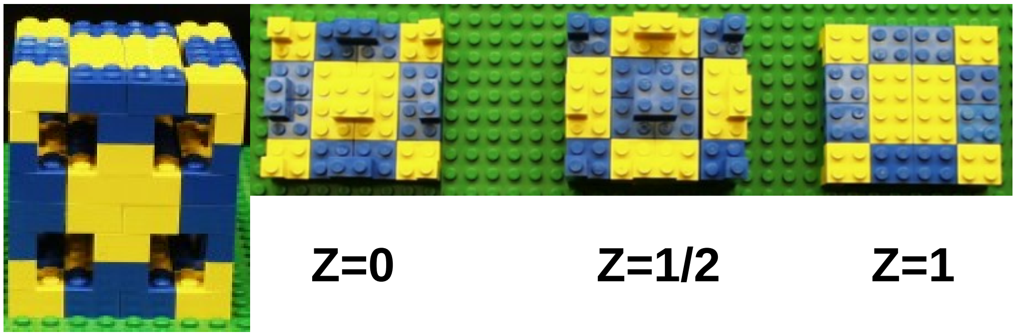

Figure 1.12 - The actual unit cell of the sodium chloride structure depicted in Figure 1.8 (middle) and Figure 1.9 built with fractional atoms, as well as the layer sequence for its construction, built from:

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.

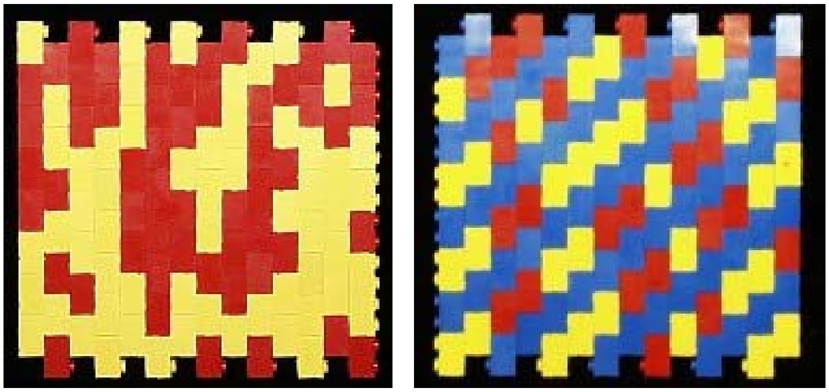

Figure 1.13 - Models of random solid solutions produced by 1x2 bricks.

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_xAs_{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.

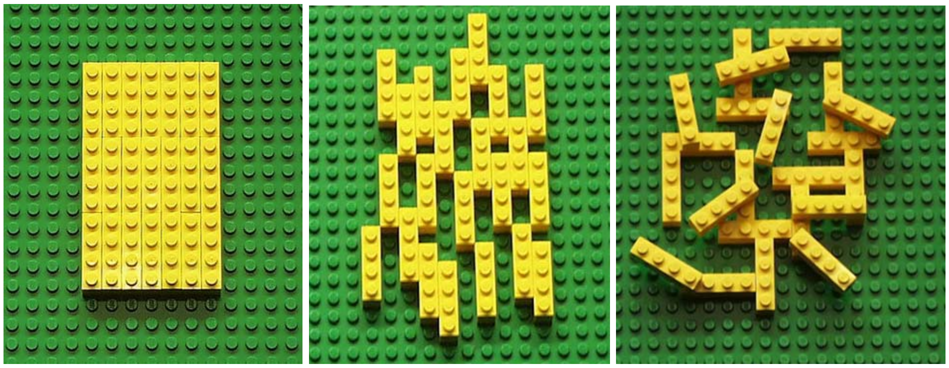

Figure 1.14 – (left to right) 1x4 LEGO® brick representations of a crystalline solid, one type of a liquid crystal phase, and a liquid.

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.

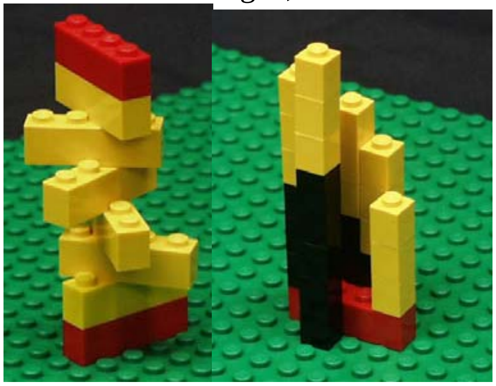

Figure 1.15 – (left) LEGO® bricks arranged to represent the cholesteric liquid crystal of a chiral molecule. (right) LEGO® bricks arranged to represent the charged molecules above under the influence of an electric field. Their orientation has been changed and light is no longer transmitted through the 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.

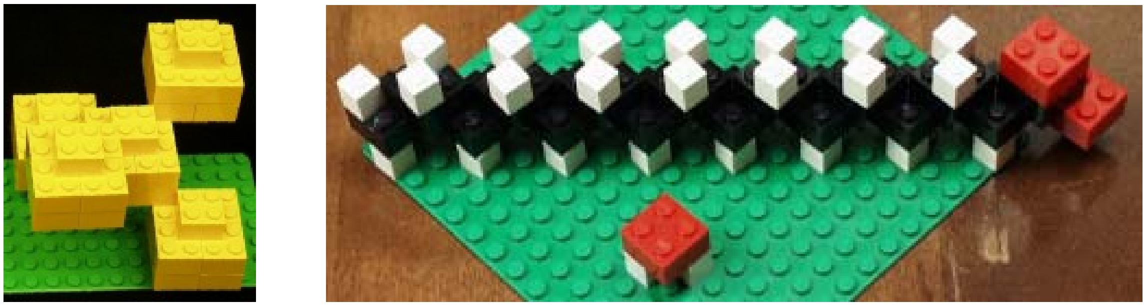

Figure 1.16 – (left) Representation of a tetrahedral arrangement of atoms with five clusters of two 2x2 bricks and four 2x4 bricks. (right) Representation of palmitic acid anion and a water molecule. Like the color coding of many organic chemistry models, the 16 black 2x2 bricks represent carbon atoms,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

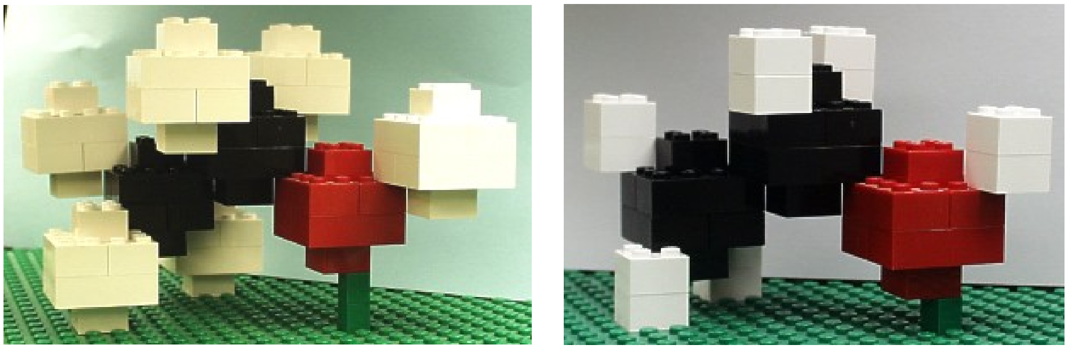

Figure 1.17 – Two representations of an ethanol (C_2H_6O) molecule. Like many organic chemistry models: black = carbon, white = hydrogen, red = oxygen. (left) All atoms are comprised of clusters of two 2x2 bricks and four 2x4 bricks. (right) The hydrogen atoms have been changed to smaller clusters of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

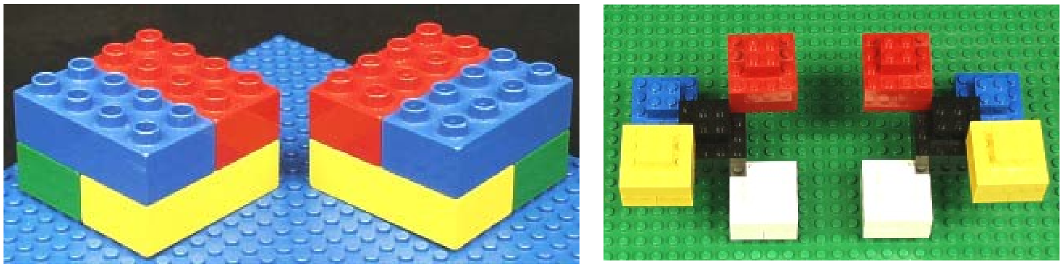

Figure 1.18 – Chiral structures using (left) 2x4 bricks or (right) clusters of two 2x2 bricks and four 2x4 bricks.