A Mathematical Analysis of Zeolites

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Abstract

Zeolites are naturally occurring minerals consisting of simple building blocks which mathematically correspond to tetrahedra. As a purely combinatorial concept, $n$-dimensional zeolites may be defined as line graphs of $(n + 1)$-regular graphs. Not all combinatorial zeolites have geometric realizations. We introduce the layer construction to obtain an $(n + 1)$-dimensional geometric zeolite from an $n$-dimensional one. By interpreting the Harborth graph as a finite 2-dimensional geometric zeolite, we obtain, using the layer construction, a finite 3-dimensional geometric zeolite, which might be synthesized.
Executive Summary

Zeolites are minerals that grow on rocks and other places where volcanic activities are prominent. They are also characterized as crystals. Zeolites are made of SiO$_4$ molecules. Geometrically, this arrangement of atoms has a tetrahedral structure. Zeolites are also synthesized in the laboratory, and are often used as microfilters.

We look at zeolites from a geometry and a combinatorial standpoint. A geometric zeolite is viewed as a saturated packing of tetrahedra. Combinatorially, zeolites are line graphs of four-regular graphs.

In general, we define an $n$-dimensional combinatorial zeolite as the line graph of an $(n + 1)$-regular graph. We proceed to ask: given a $n$-dimensional combinatorial zeolite, can we construct it in $n$-space in such a way that all edges have the same length, and no two simplices intersect?

For dimension one, we are able to show that there exists one solution. For dimension two, we provide some infinite and finite examples.

We present the layer construction to construct an $(n + 1)$-dimensional geometric zeolite from an $n$-dimensional one. We use the Harborth graph to obtain a three-dimensional geometric finite zeolite, and also an infinite geometric zeolite, which is cylindrical. We note that this mathematical construct shares many features with the naturally occurring zeolites.

Since a two-dimensional combinatorial zeolite is a four-regular graph, the line graph construction is another way to obtain a three-dimensional combinatorial zeolite from a two-dimensional one, but this combinatorial construction does not give information about the geometric realizability. We assemble the tetrahedral packing corresponding to the line graph of the Harborth graph and conjecture that it has a unit distance realization in three-space; however, it might not be an embedding.
Acknowledgments

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1 What are Zeolites?

Zeolites are naturally occurring minerals that have a crystalline structure. After being discovered over 200 years ago (see section 1.1), zeolites have been researched by chemists and chemical engineers who strive to better understand them. They have proved to be useful in different ways (see section 1.3) and continue to make an impact in our world today.

1.1 History and Geology

Zeolites were discovered in 1756 by Swedish mineralogist Axel Frederick Cronsted. After heating the zeolites, he observed that only steam came out. As a result of this observation, he named them zeolites. The word comes from two Greek words: “zeo” which means “to boil” and “lithos” which means “stone” [1]. These minerals are found on surfaces, such as: chemical sedimentary rock, metamorphic rock, and places near volcanic activity [2].

1.2 Structure and Properties

In nature, zeolites have four oxygen molecules that are attached to either an aluminum or silicon atom [3]. So the molecular structure is $\text{AlO}_4$ or $\text{SiO}_4$. By connecting the oxygen atoms with a line, the resulting object is a tetrahedral structure. The basic molecular structure of a zeolite is shown in figure 2a and a tetrahedral structure is shown in figure 2c. Due to their chemical structure, zeolite molecules are limited on how they interact with each other. When two zeolite molecules interact, they can only have one common point. In terms of a tetrahedral structure, two tetrahedra can only share one vertex [4]. The way that zeolite molecules interact causes them to have large empty spaces in between the molecules. These empty spaces are called pores and they are important in a zeolite’s ability to adsorb chemicals [5]. Furthermore, the zeolite’s structure makes it useful in other areas such as: filters [6], and catalysts [7] (see section 1.3). In figure 2d, one can see five pores of the zeolite MFI. On figures 2a, 2b and 2b, the gray atom is either silicon or aluminum and the red atoms are oxygens.
1.3 Common Uses

Due to their large pores, zeolites are mainly used for filters; so, when liquid passes through the zeolite, the impurities get trapped in it. Zeolites have been primarily used in filtering water but it is also used in filtering other liquids as well [6]. Zeolites are also used for adsorbing chemicals that are dangerous to the environment; zeolites, for example, have been used in treating radioactive liquid waste in Turkey [8]. Also, by adding zeolite powder to the tobacco in cigarettes, some carcinogenic agents can be reduced by up to 80 percent [9]. In the field of agriculture, zeolites are used for tasks such as: removing odor, slowly spreading fertilizers and pesticides, drying and storage of grain, and more [5]. As catalysts, zeolites have been used in the refinement process that gasoline must go through before it can be useful [10].

1.4 Diversity of Zeolites

1.4.1 Natural Zeolites

Zeolites were originally discovered as naturally occurring minerals. As mentioned before (see section 1.1), they mainly grow on rocks but also on places where volcano activity has taken place [2]. From the discovery of the first zeolite, in 1756, until now, scientists were able to discover about 40 other kinds of natural zeolites [11]. In 2001, during the 13th International Zeolite Association (IZA) in Montpellier, France, the IZA formed a Commission on Natural
Zeolites. The Commission strives to primarily establish rules for characterizing natural zeolites, and to write and maintain a database on natural zeolites \cite{12}. The Commission on Natural Zeolites has a database on all the currently existing natural zeolites and for each natural zeolite they maintain information such as: physical properties, facts on the crystallography, name, origin, a careful description of the crystal structure, and where the zeolite can be found \cite{13}.

1.4.2 Synthetic Zeolites and Zeolite Synthesis

Although zeolites were first found in nature, today they can also be synthesized in a laboratory. The first person to begin experimenting with the synthesis of new zeolites was St. Clair Deville in 1862; however, it wasn’t until the late 1940s that the production of zeolites increased. First, only inorganic components were used in the synthesis of zeolites, but starting in 1961, a variety of organic and inorganic components were used in chemical reactions \cite{14}. These synthetic zeolites have the same structure as naturally occurring ones but they may also have other elements and molecules like sodium, ammonium ions and others that naturally occurring zeolites do not have \cite{11}. Today, there exist about 200 different kinds of zeolites and most of them are synthetic \cite{15}.

When zeolites were first synthesized most of the work was completed by normal chemical reagents. Today, however, the process of synthesizing zeolites is completely different. First, “silicate and aluminate solutions or sols” are mixed to form aluminosilicate gels \cite{16}. Then, these aluminosilicate gels are placed in a hydrothermal system which crystallizes the gels, turning them into zeolites. In order to get different types of zeolites through the same process, chemists will perform some changes in the following areas: the composition of the aluminosilicate gels, the temperature in the hydrothermal system, and the time the zeolites are left in the hydrothermal system to crystallize \cite{17}.

1.5 International Zeolite Association

Due to the rapidly increasing number of known zeolites, people needed a way to document all of them. The International Zeolite Association (IZA) was organized in 1973 and their main goal is to record and document new zeolites that are being synthesized \cite{15}. This database looks at each different type of zeolite and documents their characteristics.

1.6 Classifying Synthetic Zeolites

Because of the great advancements in zeolite synthesis, chemists have also found a need to classify these zeolites. The primary reasons for classifying them are: to make the data available to scientists, and to facilitate the process of identifying relationships between different zeolites \cite{18}. Scientists have come up with a systematic process to classify zeolites and in the process they also identify various components of the zeolite. Some of the most important components of a synthetic zeolite are described below (see sections \ref{16.1} through \ref{16.12}). All the information is taken from the Atlas of Zeolite Framework Types \cite{19}, unless stated otherwise.
1.6.1 Nomenclature

Zeolites are named by the IZA Structure Commission. Each zeolite is given a name which can be based on either its chemical make-up or the place where it was first made (usually an university, research facility or a company). Also, zeolites are given a three-letter combination which is called the zeolite code. The letters in the zeolite code usually come from the first letter corresponding to the words that make up the zeolite’s full name.

1.6.2 Space group

The space group is a mathematical term that refers to the symmetry of the zeolite. Chemists will look at the symmetry of each zeolite and record the symmetry group that is associated with each zeolite. In the IZA database, the Hermann-Mauguin notation is used to show the space groups that each zeolite belongs to. The Hermann-Mauguin notation is a notation where each type of symmetry is denoted by a letter and each combination of letters represents the space group of the object.

1.6.3 Cell Parameters

The cell parameters of a zeolite are the dimensions associated with every framework type. In order to obtained the given parameters, chemists use the ideal SiO$_4$ composition of a zeolite. The following measurements are the distances and weights that correspond to a given combination of silicon and oxygen interactions:

\[
\begin{align*}
 d_{\text{Si-O}} &= 1.61\text{Å} & \text{weight} &= 2.0 \\
 d_{\text{O-O}} &= 2.629\text{Å} & \text{weight} &= 0.61 \\
 d_{\text{Si-Si}} &= 3.07\text{Å} & \text{weight} &= 0.2 
\end{align*}
\]

Chemists also define parameters that refer to the crystalline property of zeolites as they are built on a lattice (see section 1.7.2). These properties are: the direction vectors \((a, b, c)\) and the angle between vectors \((\alpha, \beta, \gamma)\). For more information on the lattices see section 1.7.2.

1.6.4 Framework Density

The framework density (FD) of a zeolite is defined to as “the number of tetrahedrally coordinated framework atoms (T-atoms) per 1000 Å [Angstroms]” [19]. In other words, they are classified by how tightly packed the tetrahedra are. The standard FD range for zeolites is between 12.1 and 20.6 T-atoms per 1000 Å. The FD of a zeolite can also be a range of numbers, rather than a specific number. Some reasons for the variance in FD are: the zeolite’s flexible attributes, the different types of materials used and the chemical composition. In the case when zeolites are able to expand, chemists will usually calculate the FD for a zeolite when it is expanded.
1.6.5 Coordination Sequences

The concept of coordination sequences (CS) is useful for calculating a zeolite’s topological density. The CS is calculated by counting the number of interactions that can exist between T-atoms. For a normal zeolite framework each T-atom is connected to at most 4 other T-atoms. First, only one SiO$_4$ molecule exists and since there are 4 oxygen molecules, that means 4 possible bonds; this is denoted by $N_1 = 4$. Now, each of those 4 oxygen molecules can be linked to other T-atoms; so in this level there at most 12 T-atoms, and is denoted by $N_2 = 12$. The process continues where each of those 12 oxygen molecules can be connected to other T-atoms. The pattern follows the equation:

$$N_k \leq 4 \cdot 3^{k-1}$$

where $k = 1, 2, ...$

and $k$ denotes the number of levels traveled outside of the initial T-atom. Also, it is important to note that this equation only shows the maximum number of T-atoms that could exist. The reason for this is because as the number of T-atoms increases, they may form rings and the T-atoms may share oxygen molecules.

1.6.6 Topological Density

The topological density of a zeolite is calculated directly from the coordination sequence. It has been shown that the CS of a zeolite follows a quadratic formula [20]:

$$N_k = a_i k^2 + b_i k + c_i$$

where $k = i + Mn$, $n = 0, 1, 2, ..., i = 1, 2, 3, ..., M$ and $M$ is the total number of equations. However, once the limit is taken as $k$ goes to infinity, only the term $ak^2$ matters. So, chemists calculate the topological density “as the mean of all $ai$ divided by the dimensionality of the topology”. The dimensionality of zeolites is 3, so the topological density is:

$$TD = \frac{<a_i>}{3} = \frac{1}{3p} \cdot \sum_{i=1}^{p} a_i$$

Since calculating the sum can be time consuming, the mean of all $ai$ has been approximated into two different ways. The first way that the mean is approximated is from “the last 100 terms of a CS with a 1000 terms”. This is called the TD1000:100, and the value is about ±0.001. The other approximation is TD$_{10}$ which uses the sum of the values for $N_0$ to $N_{10}$. This approximation is not very accurate and the difference between the TD$_{10}$ and TD1000:100 can be very different; therefore, the TD1000:100 is the preferred method of approximating the mean of $a_i$.

1.6.7 Ring Sizes

The ring sizes of a zeolite is based on the way that the zeolite is constructed; they are described as the closed loops in the zeolite. The ring size is the number of sides a ring has. Zeolites can have a range of different ring sizes.
1.6.8 Channel Systems
Channels are cylindrical holes in zeolites (see figure 2d).

1.6.9 Maximum Diameter of a Sphere
The maximum diameter of a sphere that can get through a zeolite gives information about
the size of the channels in the zeolite. This section is usually broken into two parts. The first
part is the “diameter of the largest possible included sphere” [15]. This means that there is
space inside the zeolite for such a sphere. The second part of information is “the diameter
of the largest-free-sphere that can diffuse along a [or b or c]” [15]. This means that given
any channel in a specific direction, such a sphere can get though the channel.

1.6.10 Accessible Volume
A measure for the empty space inside a zeolite.

1.6.11 Secondary Building Units
Secondary building units (SBU’s) refer to the framework of a zeolite. SBU’s are described as
the smallest building units of a zeolite which can be used to build the zeolite as a whole. A
zeolite can have more than one secondary building unit as long as each individual unit can
be used to construct the whole zeolite. Another important fact about SBU’s is that they are
made up of at most 16 T-atoms. Furthermore, they are always symmetrical.

1.6.12 Composite Building Units
Composite building units (CBU’s) are similar to SBU’s. They are similar in that they are
small subunits of a zeolite. However, unlike SBU’s, composite building units can not be used
to build the entire zeolite and they are not required to be symmetrical. A zeolite can have
multiple composite building units and all these units arranged together will form the whole
zeolite.

1.7 Crystals
Zeolites are mainly labeled as minerals, but they are also in the crystal family. In short,
crystals are structures that repeat throughout space and form patterns. Each different type
of zeolite makes its own specific pattern that can be observed and studied.

1.7.1 Structure
In chemistry, crystals are described as being “made up of a regular arrangement of atoms in
a pattern that repeats itself in all three spatial dimensions” [21]. In other words, crystals are
a collection of atoms and molecules that are arranged in a specific pattern and this pattern
repeats in all directions. Since crystals are made up of atoms they are subject to temperature.
When crystals are heated up, the atoms might grow farther apart from each other slightly
and when they are cooled to lower temperatures, they become more tightly packed [22].
This property allows crystals to have some range of motion. They will always have the same pattern but the distances between atoms may vary to some degree. Additionally, because crystals are repeated in space, they are symmetrical objects [22]. This symmetrical property has been of great interest to mathematicians who strive to understand all possible types of symmetry.

1.7.2 Lattices

As stated before (see section 1.7.1), one of the most important parts of a crystal is its symmetry. Crystals are usually drawn on a lattice. A lattice “is the geometrical image of the operation of the translation operators on the node at the origin” [22]. The unit cell of a crystal is defined as the part of the crystal that is repeated in all directions; on a lattice, this is often denoted by placing a dotted line around the unit cell. [22].

In any two-dimensional lattice there are three parameters: vector \( a \), vector \( b \), and an angle \( \gamma \). The vectors \( a \) and \( b \) refer to the different distances and the angle \( \gamma \) refers to the angle between \( a \) and \( b \). There are 4 different lattices in two-dimensional space. Table 1 summarizes the four different lattices that can be found in two dimensions.

<table>
<thead>
<tr>
<th>Name</th>
<th>Vector</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square</td>
<td>( a = b )</td>
<td>( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Rectangular</td>
<td>( a \neq b )</td>
<td>( \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Hexagon</td>
<td>( a = b )</td>
<td>( \gamma = 120^\circ )</td>
</tr>
<tr>
<td>Oblique</td>
<td>( a \neq b )</td>
<td>( \gamma \neq 120^\circ, \gamma \neq 90^\circ )</td>
</tr>
</tbody>
</table>

Unlike two-dimensional lattices, a three-dimensional lattice contains 6 parameters: vector \( a \), \( b \), \( c \), and angles \( \alpha \), \( \beta \), \( \gamma \). The parameters \( a \), \( b \), and \( c \) refer to the different distances. The parameter \( \alpha \) refers to the angle between vectors \( b \) and \( c \), the parameter \( \beta \) refers to the angle between vectors \( a \) and \( c \), and the parameter \( \gamma \) refers to the angle between vectors \( a \) and \( b \). In three-dimensional space, there are 7 different lattices. Table 2 shows all the possible lattices for the three-dimensional space.

<table>
<thead>
<tr>
<th>Name</th>
<th>Vector</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>( a = b = c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>( a \neq b \neq c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>( a \neq b \neq c )</td>
<td>( \alpha = \beta = \gamma = 90^\circ )</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>( a \neq b \neq c )</td>
<td>( \alpha = \beta = 90^\circ, \gamma = 120^\circ )</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>( a = b = c )</td>
<td>( \alpha = \beta = \gamma )</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>( a \neq b \neq c )</td>
<td>( \alpha = \gamma = 90^\circ, \beta \neq 90^\circ )</td>
</tr>
<tr>
<td>Triclinic</td>
<td>( a \neq b \neq c )</td>
<td>( \alpha \neq \beta \neq \gamma )</td>
</tr>
</tbody>
</table>
1.7.3 Groups

Since crystals are symmetrical, it is important for mathematicians to know in which ways crystals are symmetrical. They strive to know the kinds of operations that can be done to crystals without violating its symmetry. For more see section 2.1.

1.7.4 Tiling

An important application of two-dimensional lattices is in the field of tiling. Tiling is covering a plane with pieces without overlapping tiles or leaving gaps. The pieces used in tiling are called tiles. These tiles can be placed in any way as long as it follows the rules for tiling. Sometimes, additional restrictions can be added to the rules of tiling that would restrict the type of tiles used [22].

Natural tiling is a specific type of tiling. Natural tiling refers to tiling a dimension with regular shapes. In dimension two, it is clear that there are three different tiles can cover the plane; for two dimensions, the natural tiles are: the triangle, the square, and the hexagon. For three-dimensional space, a natural tile is the cube.

1.8 Zeolites in Mathematics

Any molecule may be studied mathematically using “combinatorial information” such as: which atom is bonded to which other atom, or using geometry by considering interatomic distances and bond angles. By viewing the molecule or crystal as a geometric constraint system, one can study or predict its rigidity, its shape and its internal degree of freedom.
2 Mathematical Background

2.1 Groups

French Mathematician, Évariste Galois (1811-1832) is considered to be one of the founders of group theory and is credited for naming a group in the mathematical sense still in use today. In 1830, Galois used the term “group” to refer to a finite set together with a binary operation such that certain conditions are satisfied. We give these definitions below.

Definition 1. Let \( G \) be a set. A binary operation on \( G \) is a function that assigns each ordered pair of elements of \( G \) an element of \( G \).

A group is formed when a binary operation is coupled with a domain, and the following conditions are satisfied:

Definition 2. Let \( G \) be a set together with a binary operation (usually called multiplication) that assigns to each ordered pair \((a, b)\) of elements of \( G \) an element in \( G \) denoted by \( a \cdot b \). We say \( G \) is a group under this operation if the following four properties are satisfied:

- **Closure**: The set is closed under the operation (i.e. if \( a, b \in G \), then \( a \cdot b \in G \))
- **Associativity**: The operation is associative (i.e. \( a \cdot (b \cdot c) = (a \cdot b) \cdot c \))
- **Identity**: There exists an identity \( e \) such that: \( e \cdot a = a = a \cdot e \)
- **Inverses**: For every element \( a \) in \( G \), there is an element \( b \) such that: \( a \cdot b = b \cdot a = e \)

If in addition \( a \cdot b = b \cdot a \) for all elements in the set \( G \), then the group is called abelian, after the Norwegian mathematician Niels Abel.

2.1.1 Permutation Groups

An important group is the permutation group.

Definition 3. A permutation of a set \( A \) is a function from \( A \) to \( A \) that is both one-to-one and onto. A permutation group of a set \( A \) is a set of permutations of \( A \) that forms a group under function composition.

2.1.2 Symmetric Group

The symmetric group is an important that follows from the permutation group.

Definition 4. Let \( A = \{1, 2, \ldots, n\} \). The set of all permutations of \( A \) is called the symmetric group of degree \( n \) and is denoted by \( S_n \).

We can easily count the number of permutations in the symmetric group. We see that for the first element, we can map it to \( n \) different places, the second element can be mapped to \( n - 1 \) places, until the last element which can only be mapped to one place. We conclude that the total number of possible permutations in \( S_n \) is \( n! \).
2.1.3 Group Acting on a Set

Definition 5. An isomorphism \( \phi \) from a group \( G \) to a group \( \bar{G} \) is a one-to-one mapping (or function) from \( G \) onto \( \bar{G} \) that preserves the group operation. That is, \( \phi(a \cdot b) = \phi(a) \cdot \phi(b) \) for all \( a, b \in G \) [23].

Theorem 1 (Cayley’s Theorem). Every group is isomorphic to a group of permutations [23].

Cayley’s theorem states that any group can be written as a permutation group. This is important because when defining the symmetry of an object, we can easily write it as a set of permutations on that object.

2.1.3.1 The Orbit of an Element

Let \( G \) be a group acting on a set \( S \). Then we can specify, for each element of \( S \), an orbit under the group action.

Definition 6. Let \( G \) be a set of permutations on a set \( S \). For each \( i \) in \( S \), let \( \text{orb}_G(i) = \{ \phi(i) | \phi \in G \} \). The set \( \text{orb}_G(i) \) is a subset of \( S \) called the orbit of \( i \) under \( G \). We use \( |\text{orb}_G(i)| \) to denote the number of elements in \( \text{orb}_G(i) \) [23].

If we consider a regular polygon with \( n \) vertices, the size of the orbit of a vertex \( \alpha \) of is \( n \). By rotating the polygon, vertex \( \alpha \) visits all the other vertices in the polygon. The orbit of \( \alpha \) is the position of all the other vertices.

2.1.3.2 The Stabilizer of an Element

Let \( G \) a group acting on a set \( S \), then the group elements that fix a certain element form a subgroup.

Definition 7. Let \( G \) be a group of permutations of a set \( S \). For each \( i \) in \( S \), let \( \text{stab}_G(i) = \{ \phi \in G | \phi(i) = i \} \). We call \( \text{stab}_G(i) \) the stabilizer of \( i \) in \( G \) [23].

In other words, the stabilizer of a point \( i \) is the set of permutations that leave \( i \) alone. In a regular polygon with \( n \) vertices, the stabilizer of a vertex \( \alpha \) are the identity, and reflection about the axis that passes through \( \alpha \).

2.1.3.3 The Orbit-Stabilizer Theorem

A good understanding of orbits and the stabilizer of a point leads to a fast understanding of the symmetry group of any shape.

Theorem 2 (Orbit-Stabilizer Theorem). Let \( G \) be a finite group of permutations of a set \( S \). Then, for any \( i \) from \( S \), \( |G| = |\text{orb}_G(i)| \cdot |\text{stab}_G(i)| \) [23].

This theorem states that the size of the group is equal to the size of the orbit of a point times the size of the stabilizer of that point. When trying to compute the order of large symmetry groups, the orbit-stabilizer theorem can be quite helpful. In the next few sections, the symmetry group of some simple geometric objects will be explained and this theorem will be used.

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2.1.4 Examples of Symmetry Groups

2.1.4.1 The Symmetry Group of a Triangle

Since the equilateral triangle is the smallest regular polygon, it is easy to visualize its symmetry group. First, consider the rotational symmetry of the triangle. The rotational symmetry group of the triangle includes the rotation by 120 degrees, and by 240 degrees. We define the identity to be leaving the triangle untouched, which is equivalent to a rotation by 0 or 360 degrees.

The other form of symmetry in a triangle comes from reflections. An equilateral triangle can be reflected across three different axes. If each angle is bisected (divided into two equal parts) by a line, those lines represent the axis of reflection. Figure 3 shows the three rotations and the three reflections of a triangle. Table 3 shows the group table for the symmetry group of the triangle, which is isomorphic to $S_3$ (see section 2.1.2).

![Figure 3: Symmetry Group of a Triangle](image)

<table>
<thead>
<tr>
<th></th>
<th>Id</th>
<th>$R_{120}$</th>
<th>$R_{240}$</th>
<th>$M_a$</th>
<th>$M_b$</th>
<th>$M_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Id</td>
<td>Id</td>
<td>$R_{120}$</td>
<td>$R_{240}$</td>
<td>$M_a$</td>
<td>$M_b$</td>
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</tr>
<tr>
<td>$R_{120}$</td>
<td>$R_{120}$</td>
<td>$R_{240}$</td>
<td>Id</td>
<td>$M_b$</td>
<td>$M_c$</td>
<td>$M_a$</td>
</tr>
<tr>
<td>$R_{240}$</td>
<td>$R_{240}$</td>
<td>Id</td>
<td>$R_{120}$</td>
<td>$M_c$</td>
<td>$M_a$</td>
<td>$M_b$</td>
</tr>
<tr>
<td>$M_a$</td>
<td>$M_a$</td>
<td>$M_c$</td>
<td>$M_b$</td>
<td>Id</td>
<td>$R_{240}$</td>
<td>$R_{120}$</td>
</tr>
<tr>
<td>$M_b$</td>
<td>$M_b$</td>
<td>$M_a$</td>
<td>$M_c$</td>
<td>$R_{120}$</td>
<td>Id</td>
<td>$R_{240}$</td>
</tr>
<tr>
<td>$M_c$</td>
<td>$M_c$</td>
<td>$M_b$</td>
<td>$M_a$</td>
<td>$R_{240}$</td>
<td>$R_{120}$</td>
<td>Id</td>
</tr>
</tbody>
</table>

Table 3: Symmetry Group of a Triangle
vertices in the triangle. So, the size of the orbit of a vertex is three. Now, we look at the stabilizer of that same vertex. There are two stabilizers for any vertex, namely, the identity and the reflection about the axis that goes through that vertex. The orbit-stabilizer theorem says that the size of a group is equal to the size of the stabilizer multiplied by the size of the orbit of any element; we have, \(2 \cdot 3 = 6\). So the symmetry group of the triangle is 6, which is exactly what we calculated before.

The orbit-stabilizer theorem can also be applied to an edge. The edge \(ab\) can be moved to three different locations: stay unchanged, or move to the location of the other two edges. We have the size of the orbit of the edge \(ab\) is 3. In order to stabilize the edge \(ab\), two operations can be performed: the identity and reflecting the triangle across the line that goes through the edge \(ab\) and vertex \(c\). The size of the stabilizer of the edge is 2. Again we have \(2 \cdot 3 = 6\), confirming our result.

### 2.1.4.2 The Symmetry Group of a Square

The square is a regular polygon where \(n = 4\) which means that its symmetry group involves rotations and reflection. The four rotations are: rotation by 90 degrees, by 180 degrees, by 270 degrees, and the identity. The four reflections are: about the vertical axis, about the horizontal axis, and about the two diagonals. Therefore, the symmetry group of the square is 8. Figure [4] shows the symmetry group of the square.

If we apply the orbit-stabilizer theorem, we find the size of the orbit and the stabilizer of a vertex or edge. The orbit of a vertex or edge is found through the rotations of the square; the square has four rotations and each rotation takes a vertex or edge and sends it to a different location in the square. To stabilize a vertex, there are two possible ways to accomplish this: the identity and reflecting the square along the diagonal that passes through the stabilized vertex. To stabilize an edge, there are also two ways, namely: the identity and either a vertical or horizontal reflection. We have that the size of the orbit is 4, and the size of the stabilizer is 2 (in both cases), and \(4 \cdot 2 = 8\). Therefore, the symmetry group of the square is 8.

### 2.1.4.3 The Symmetry Group of a Tetrahedron

Now, we consider the symmetry group of a tetrahedron. A tetrahedron is a pyramid with a triangular base.

First, we find the orbit of a vertex. A tetrahedron has 4 vertices, so the size of the orbit of a vertex of a tetrahedron is 4. Now, we calculate the size of the stabilizer of that vertex. We let the stabilized vertex be the one that is at the top, above the \(xy\)-plane. We draw a line that passes through the stabilized vertex of the tetrahedron and the triangular base below. We can rotate the tetrahedron around that line. The top vertex is stabilized and there are three rotations that can be performed: rotation by 120 degrees, by 240 degrees and 360 degrees which is the identity. The next three operations that stabilize a vertex are reflections. Again, we let the stabilized vertex be the one that is above the \(xy\)-plane.
To stabilize this point, a plane of symmetry can be drawn such that it goes through the stabilized vertex and a vertex that is on the $xy$-plane. Since there are three vertices that are parallel to the $xy$-plane, there is a reflection for each of the vertices on the $xy$-plane. Therefore, the size of the stabilizer of a point is 6. Since $4 \cdot 6 = 24$, then the size of the symmetry group of a tetrahedron is 24, which is equivalent to $|S_4|$ (since $|S_4| = 4\cdot 3 \cdot 2 \cdot 1 = 12$).

2.1.4.4 Symmetry Group of a Cube

For the previous two examples, it was possible to calculate by hand the symmetry group of each object, since they were small. The symmetry group of cube, however, has a larger number of vertices, edges and faces, so we will use the orbit-stabilizer theorem to calculate the size of its symmetry group.

First, consider the orbit-stabilizer theorem applied to a vertex. A cube has 8 vertices; therefore, the size of the orbit of a vertex is 8 because there exists some permutation that can take a vertex to any other vertex. Now, consider the stabilizer of a vertex. The first way to fix a vertex is by the identity. The second way to stabilize a vertex is through rotation. The rotational axis is the line that goes through the stabilized vertex and the vertex that is directly opposite of the stabilized vertex (when this is done, the cube has its stabilized vertex pointing up). With this rotational axis, the vertex is stabilized when the cube is rotated by 120 degrees, by 240 degrees and by 360 degrees which is the identity. The next three ways to stabilize a vertex is through reflection across a plane. The planes that stabilizes a vertex are the planes that passes through the stabilized vertex and through the diagonal of the faces that touch the stabilized vertex. We have that the orbit of a vertex is 8 and the stabilizer of a vertex is 6, so the order of the symmetry group of the cube is 48 (i.e. $8 \cdot 6 = 48$).

Now, consider the orbit-stabilizer theorem applied to an edge. A cube has 12 edges; therefore, the size of the orbit of any edge is 12, because there exists some permutation that can take an edge to any other edge. Next, consider the stabilizer of an edge. The first way that
we can stabilize an edge is by drawing a line that goes through the midpoint of the stabilization edge, and rotating the cube by 180 degrees about that line. Reflection is the second way to stabilize an edge. The reflections that will stabilize the edge are: reflection on a vertical plane that crosses the stabilized edge, and the reflection across the diagonal plane that goes through the given edge. The last stabilizer of the edge is the identity; so, there are 4 operations that stabilize an edge. Multiplying the size of the orbit times the size of the stabilizer of the edge gives that order of the symmetry group is again 48.

Finally, consider the orbit-stabilizer theorem applied to a face. A cube has 6 faces, and therefore the size of the orbit of a face is 6, because there exists some permutation that can take a face to any other face. Next we find the size of the stabilizer of a face. If a line is drawn that goes through the center of the stabilized face and across the cube, then the cube can be rotated around it. This gives 4 rotations: rotation by 90 degrees, 180 degrees, 270 degrees, and 360 degrees which is the identity. Reflections across the vertical plane, horizontal plane and the two diagonal planes gives 4 more stabilizers for the face of a cube. Since $6 \cdot 8 = 48$, the order of the symmetry group of the cube is 48.

2.2 Graphs

Graph theory is an important part of the study of zeolites, and a good understanding of this part of math is essential to understanding the contents of this research.

**Definition 8.** A simple graph $G$ is a pair $(V(G), E(G))$ where $V(G)$ is a non-empty finite set of elements called vertices, and $E(G)$ is a finite set of unordered pairs of distinct elements called edges [24].

In a graph, the vertices are usually represented by points or nodes, and the edges are represented by line segments connecting the vertices. Figure 5 shows an example of a graph. We say that the degree of a vertex $v$ is the total number of edges that are incident to $v$. In particular, we say that a graph is $r$-regular if all vertices in graph have degree $r$. A graph is said to have a path from vertex $u$ to vertex $v$ if there is a set of distinct edges that connect vertex $u$ to vertex $v$. For example, in figure 5 an example of a path from vertex $u$ to vertex $v$ is $ud, dc, cv$.

A graph is said to be connected if given any pair of vertices, there is a path connecting them; if no such path exists then the graph is a disconnected graph. Furthermore, we study how well connected a graph is by looking at the number of vertices or edges required to disconnect a graph.

We define a cutset of vertices or edges of a graph $G$ to be a set of vertices or edges of $G$ that if removed, the graph would become disconnected. We say that the edge-connectivity $\lambda(G)$ is the minimum number of edges that disconnect $G$. In a similar manner, we define vertex-connectivity $\kappa(G)$ to be the minimum number of vertices in $G$ that if deleted, would result in a disconnected graph. In the case of vertex deletion, if a vertex is deleted then all edges that are incident with that vertex are also deleted. In the graph of figure 5 we see that $\lambda(G) = 2$ and $\kappa(G) = 1$. 

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We define the line graph $G'$ of a graph $G$ to be a graph where the edges in $G$ become vertices in $G'$. The vertices in $G'$ are connected by an edge if in $G$ the edges share a common endpoint. The number of vertices in the line graph of $G'$ is the same as the number of edges in graph $G$; however, the number edges in $G'$ is usually more than the number of vertices in $G$. Figure 6 shows the line graphs for some of the graphs mentioned before.
2.2.1 Planarity

Recall that a graph is a drawing that uses vertices and edges. The vertices are coordinates in 2 dimensional space and the edges are line segments that connect two vertices together.

We say that a graph is planar if it can be drawn in the plane in such a way that there are no edge crossings. We say that a graph is a plane graph if it is drawn in a planar manner. Two major theorems that arise in the area of planarity are Fary’s Theorem and Euler’s Theorem. Fary’s theorem states that if a graph is a planar graph then it can be drawn in such a way that all edges are straight line segments. Euler’s theorem states that for any connected plane graph with \( n \) vertices, \( m \) edges and \( f \) faces, then \( n - m + f = 2 \). It is important to remember that when counting the number of faces in a graph, there is always the additional outside face. We show how Euler’s Theorem can be applied to a tetrahedron and a cube.

First, consider the graph of a tetrahedron. This graph contains 4 vertices, 6 edges and 4 faces (3 inner faces and 1 face that surrounds the entire tetrahedron). If we use these numbers in Euler’s theorem, we get \( 4 - 6 + 4 = 2 \). Now we consider graph of a cube. The cube graph contains 8 vertices, 12 edges, and 6 faces. Again the result is \( 8 - 12 + 6 = 2 \) which satisfies Euler’s Theorem.
3 Combinatorial Zeolites

Now we will define a zeolite in the mathematical context. First, we have a combinatorial zeolite. We will consider some combinatorial zeolites in the dimensions one, two and three.

Definition 9. An $n$-dimensional combinatorial zeolite is the line graph of an $(n+1)$-regular graph.

3.1 One-Dimensional Zeolites (Combinatorial)

A one-dimensional zeolite is the line graph of a two-regular graph. We know that any two-regular connected graph is a cycle. For a one-dimensional zeolite we can have an infinite path, or any cycle graph. Figure 7 shows the infinite one-dimensional combinatorial zeolite. Figure 8 shows a two cycle graphs that are finite one-dimensional combinatorial zeolite.

![Figure 7: Infinite One-Dimensional Combinatorial and Geometric Zeolite](image)

(a) Five-Cycle  
(b) Six-Cycle

![Figure 8: Finite One-Dimensional Combinatorial Zeolites](image)

3.2 Two-Dimensional Zeolites (Combinatorial)

A two-dimensional zeolite is the line graph of a three-regular graph. Figures 9 and 10 show two different two-dimensional zeolites. We can compare face sizes in a graph with the holes in the line graph construction. The holes in the line construction are the rings that are mentioned in section 1.6.7. We see that for every face of size $x$ in an $n$-regular graph, there will be a ring of size $x$ in the line graph. We can look at the size of each face in a three-regular graph and determine the ring size in the zeolite construction.

For figure 10 we can make another remark. First, there are two regular hexagons, one inside the other and respective vertices are adjacent. Also, there are two faces of length six and six faces of length four. We can generalize this to $n$-gons. If we create a graph in a similar manner with an $n$ sided polygon, we will have two faces of length $n$ and $n$ faces of length
If we consider the limit as $n$ approaches infinity, we will have the graph of an infinite ladder. This would be an example of an infinite two-dimensional zeolite. Furthermore, other examples of infinite two-dimensional zeolite are the infinite three-regular tree, and the hexagonal tiling (see section 4.2.1.2).

3.3 Three-Dimensional Zeolites (Combinatorial)

A three-dimensional zeolite is the line graph of a four-regular graph. Figures 11 and 12 show two different three-dimensional zeolites. We notice that the correlation between face sizes in the graph is equal to ring sizes in the line graph can also be applied to a four-regular graph.
Also, similar to two-dimensional combinatorial zeolites, a three-dimensional combinatorial zeolite can also be infinite. Some examples of infinite zeolites come from a four-regular tree and the square tiling (see section 4.3.1.1).

Figure 11: Example 1: Four-Regular Graph and its Line Graph

Figure 12: Example 2: Four-Regular Graph and its Line Graph
4 Geometric Zeolites

In this section, we seek to answer the following question: is it possible to create a unit distance representation of a zeolite in the correct dimension? We consider a geometric zeolite.

Definition 10. An $n$-dimensional geometric zeolite is a zeolite that can be embedded in $n$-dimension where all edges are unit length, and simplices do not overlap.

Definition 11. A simplex is $K_{n+1}$ embedded in dimension $n$ with all edges of unit length.

We will consider the different types of zeolites in all dimensions one, two and three.

4.1 One-Dimensional Zeolites (Geometric)

For a one-dimensional zeolite, the simplices are edges. The only one-dimensional zeolite is the infinite path where all vertices are on a line and the edges between the vertices have the same length. Figure 7 shows the only one-dimensional geometric zeolite.

4.2 Two-Dimensional Zeolites (Geometric)

For a two-dimensional zeolite, the simplices are regular triangles. We create a graph where all faces are triangles and each vertex of a triangle is connected to exactly one other triangle. We can also say that a two-dimensional zeolite is a saturated packing of triangles, where a saturated packing means that “vertex points are common points of the triangles and every vertex point belongs to exactly two of the triangles” [25]. We will consider some infinite and some finite two-dimensional geometric zeolites.

4.2.1 Infinite Two-Dimensional Zeolites (Geometric)

4.2.1.1 Using The Layer Construction: 1D to 2D

In general, a layer construction can be used to obtain an $(n+1)$-dimensional geometric zeolite from an $n$-dimensional zeolite. We shall create an infinite two-dimensional geometric zeolite from an infinite one-dimensional geometric zeolite.

First, consider an infinite one-dimensional geometric zeolite (as seen in figure 7). From here we can add a triangle facing down to each edge of the one-dimensional zeolites. The resulting graph is a string of triangles. We can take two of such constructions and put them together in such a way that the free vertices of the triangles are touching. In this case, we have a two-dimensional zeolite that extends infinitely in the $x$-direction (see figure 13).

We can also consider a zeolite that is slightly different. We again begin with an infinite one-dimensional geometric zeolite. Now, instead of creating triangles that all face down, we can make some triangles that face up and others that face down. We replicate this and stack them together. By doing this, we get the graph on figure 14. With this procedure, we have a two-dimensional zeolite that will extend in both the $x$ and $y$ axis. With this type of construction, we can have infinitely many two-dimensional zeolites.
4.2.1.2 Using a Combinatorial Zeolite

Though the layer construction is a sure way of obtaining a geometric zeolite from a geometric zeolite of lower dimension, not all geometric zeolites are obtained by the layer construction.

The Kagome lattice is a well-known lattice, and it is an infinite two-dimensional combinatorial and geometric zeolite. First, consider a hexagonal tiling (see figure 15a). This is a three-regular graph that can cover a two-dimensional space. Now, consider the line graph of the hexagonal tiling (see figure 15b); this is known as the Kagome lattice. Since the Kagome lattice is a saturated packing of equilateral triangles that can be replicated in the $xy$-plane, it is an infinite two-dimensional geometric zeolite.

4.2.2 A Finite Two-Dimensional Zeolite (Geometric)

The Harborth graph is an example of a finite two-dimensional geometric zeolite (see figure 16b). This graph was discovered by Heiko Harborth, a professor of mathematics at Braunschweig University of Technology in Germany. This graph is a saturated packing of triangles formed in such a way that a ring is made. We see that given the three-regular graph $F$ (see figure 16a), we can draw the line graph and we get the Harborth graph (see figure 16b). We conclude that the Harborth graph is both a geometric and combinatorial zeolite because it
is the line graph of a three-regular graph, and it can be embedded in two-dimension in such a way that simplices have unit distance and they do not overlap.

Similar to the hexagonal tiling and the kagome lattice, the holes in the Harborth graph correspond to the faces of $F$ that have the same number of sides as the holes in the Harborth graph. We show this correspondence by using Euler’s formula.

In the Harborth graph we have the following:
|V(HG)| = 63 vertices  
|E(HG)| = 126 edges  
|F(HG)| = 65 faces

We note that in the Harborth graph there are 42 faces that are shaded, and 23 faces that are holes; this including the outside face that surrounds the graph.

Now, in graph $F$, we have the following:

|V(F)| = 42 vertices  
|E(F)| = 63 edges  
|F(F)| = 23 faces

We see that the number of vertices in the Harborth graph is equal to the number of edges in $F$; this follows directly from the definition of the line graph. Next, we see that the number of holes in the Harborth graph is equal to the number of faces in $F$. We see that there is a relationship between the size of each hole in the Harborth graph and the number of faces in $F$. We notice that if there are $n$ holes in the Harborth graph with $x$ surrounding edges, then in $F$ there are $n$ faces with $x$ surrounding edges.

### 4.3 Three-Dimensional Zeolites (Geometric)

For a three-dimensional zeolite, the simplices are tetrahedra. This zeolite has the same structure as the chemical zeolite. Similar to two-dimensional zeolites, we will consider some infinite and finite geometric zeolites.

#### 4.3.1 Infinite Three-Dimensional Zeolites (Geometric)

##### 4.3.1.1 Using The Layer Construction: 2D to 3D

We can use the layer construction to get a three-dimensional zeolite from a two-dimensional zeolite. Consider figures 13 and 14, we can turn those triangles to tetrahedra facing up or down. We can replicate it and place one layer on top of the other. Depending on how the tetrahedra are made and which graph is used, we can obtain a three-dimensional zeolite that can only be replicated in either the $x$-direction, $x$ and $z$-directions, $x$ and $y$-directions, or $x$, $y$, and $z$-directions.

##### 4.3.1.2 Using a Combinatorial Zeolite

All geometric zeolites are combinatorial zeolites, but not all combinatorial zeolites are geometric. Consider a simple square grid where there is a vertex at each intersection (see figure
This graph is a four-regular graph. Now, if we take its line graph, we get the graph on figure 17b. This graph is an arrangement of tetrahedra. The vertical and horizontal lines are edges of the tetrahedron that are parallel to the \( xy \)-plane and have true length on the image. The horizontal lines are edges that are above the \( xy \)-plane, while the vertical lines are below the \( xy \)-plane. The diagonal edges are also edges of the tetrahedron but they appear shortened since they are not parallel to the \( xy \)-plane.

(a) Square Tiling

(b) Tetrahedra in 3D

Figure 17: Square Tiling and Tetrahedra in 3D

4.3.2 A Finite Three-Dimensional Zeolite (Geometric)

4.3.2.1 Using the Layer Construction: 2D to 3D

Consider the Harborth graph. We see that the Harborth graph is a plane graph and that all triangles are equilateral triangles. We can use the layer construction to turn this graph into finite three-dimensional geometric zeolite. We can turn the triangles in the Harborth graph into tetrahedra facing up. We can replicate this layer, and stack one on top of the other. If we choose all tetrahedra to face up, when we repicate it and stack them, we will a finite three-dimensional geometric zeolite that only has two layers.

We can also carefully choose some triangles in the Harborth graph to be upward facing tetrahedra and others to be downward facing tetrahedra. Figure 18 shows a possible arrangement of these tetrahedra and figure 19 shows a three-dimensional model of the graph in figure 18. In this figure, the gray triangles with the vertices in the center represent upward facing tetrahedra, and the gray triangles are downward facing tetrahedra. With this arrangement of tetrahedra, we can replicate it and stack them in such a way that the free vertices of the tetrahedra are touching. We can stack them infinitely and this becomes a three-dimensional geometric zeolite that can only be replicated in the \( z \)-direction.
4.3.2.2 Using the Combinatorial Zeolite

We noticed in section 4.3.1.2 that sometimes a zeolite can be both a geometric and combinatorial zeolite. In section 3.3 we saw that a three-dimensional combinatorial zeolite is
obtained by taking the line graph of a four-regular graph. We see from the line graph of
the Harborth graph (see figure 20b) that it is a six-regular graph; in fact, it is a saturated
packing of corner sharing tetrahedra. We ask: is there a realization of this graph Γ in three
space with all tetrahedra regular and of the same size? We will take a small portion of the
graph and show that this is in fact possible.

(a) Harborth Graph

(b) Graph Γ

Figure 20: Harborth Graph and Γ

Claim: A unit distance collection of tetrahedra from graph Γ is possible is 3-space.

Proof. First, we take three tetrahedra and we connect them in such a way that there is
a triangle in the middle (see figure 21a). Our goal is to show that if we turn the three
tetrahedra either all inward into the middle triangle or outward, we can find an angle with
the $xy$-plane such that the distance between vertices of any pairwise tetrahedron is unit
distance apart. We begin by considering when all tetrahedra are laying flat; then, if we look
at the top vertex of a tetrahedron and a vertex furthest away (the red lines in figure 21b),
that distance is greater than 1. Now, if we turn all tetrahedra inward so that all tetrahedra
collide at one point, we see that the distance is less than 1, and in fact the distance is zero.
We realize that this is a continuous motion of the tetrahedra, so by the Mean Value Theorem,
there exists some angle $\theta$ such that when all tetrahedra are positioned with angle $\theta$ with the
$xy$-plane then the distance between pairs of free vertices is equal to one.
Figure 21: Images Used in the Proof

Figure 22: Portion of the Harborth Graph and $\Gamma$
To assemble the model, we labeled each vertex in the Harborth Graph with degree four. Since we know that for each vertex of degree four in the Harborth graph there is a tetrahedron that corresponds to it, we made a drawing indicating how our model should be connected. In figure 23a we have labeled the vertices of degree four in the Harborth Graph, and figure 23b is a drawing that shows how to connect $\Gamma$. In figure 23b the additional red lines indicate that those tetrahedra must share a vertex.

![Labeled Harborth Graph](image)(a) Labeled Harborth Graph ![Gamma represented with Tetrahedron](image)(b) $\Gamma$ represented with Tetrahedron

**Figure 23: Connections of the Tetrahedra in $\Gamma$**

We used figure 23 to help us create a model of straws and twine. Figure 24 shows the end result of our model. We were able to create a model that corresponds to the graph in figure 23. We noticed that this model is flexible, but that some vertices had a tendency to go to a certain point. We were able to show that we can model one-sixth of graph $\Gamma$ in dimension three. Modeling the rest of the graph has not been attempted yet.

![Model of Part of graph $\Gamma$](image)

**Figure 24: Model of Part of graph $\Gamma$**
5 Conclusions

We have seen that crystallographers believe that a crystal should be able to expand in all three directions. We have also seen that zeolites are naturally occurring crystals, and therefore should be able to replicate in three-directions. Furthermore, we see that there are some zeolites that in nature that are needle-like (see figure 1b). Since these zeolites are needle-like, they can only be replicated in one direction. Using a layer construction of the Harborth graph, we were able to construct a zeolite that is similar to the construction of the zeolite in figure 1b. Both of these zeolite can only be replicated in one direction. Both have large pores. We conclude: maybe, the construction presented in this project is equal or very similar to the construction of naturally-occurring needle-like zeolites.
References


