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Molecular Graph Theory

Chase R. Johnson
Worcester Polytechnic Institute

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Molecular Graph Theory by Chase Johnson A Masters Project

Submitted to the Faculty of WORCESTER POLYTECHNIC INSTITUTE

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APPROVED: _____ Professor Brigitte

Servatius, Project Advisor _____

Professor Bogdan Vernescu, Head of Department

Abstract

Graph Theory is a branch of mathematics that has a wealth of applications to other science and engineering disciplines, specifically Chemistry. The primary application of graphs to Chemistry is related to understanding of structure and symmetry at the molecular level. By projecting a molecule to the plane and examining it as a graph, a lot can be learned about the underlying molecular structure of a given compound. Using concepts of Graph Theory this masters project examines the underlying structures of two specific families of compounds, fullerenes and zeolites, from a chemical and mathematical perspective.

Acknowledgements

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1 Fullerenes

1.1 Introduction

The term *fullerene* refers to a family of molecules, consisting typically of only Carbon or Boron atoms. More commonly referred to as *buckyballs*, these molecules are given this name in reference to the famous American architect Buckminster Fuller (1895-1983) who is primarily known for the design of the geodesic sphere. The name of the family is appropriate as these molecules inherently take on a spherical structure due to intermolecular forces as well as the geometry of each individual atom. The existence of a soccer-ball shaped molecule was first theorized in 1970 by Japanese chemist Eiji Osawa. Fifteen years later the first fullerene was officially discovered by a group of chemists who named it *Buckminsterfullerene*. Although not the smallest fullerene, *Buckminsterfullerene* is arguably the most famous for its impact on chemistry. Since, several other fullerenes have been discovered.

1.2 Fullerene Graphs

Fullerenes are difficult to observe in nature however their structure is well known. Utilizing Graph Theory we can better understand the underlying structure of fullerene molecules. A planar representation of a molecule is known as a *Lewis Dot Structure*. In this construction each atom is represented by its chemical symbol and these are connected with a line if they share a bond. To transform a Lewis Dot Structure into a graph we simply make every atom in the molecule a vertex in the graph with vertices sharing edges if the atoms share a bond in the molecule. Doing so we generate the graphical representations of Buckminsterfullerene C_{60} given by Figure 1. Looking at this graph we see that every vertex is connected to exactly three other vertices. Moreover, we can also see that the graphs contain only pentagonal and hexagonal faces. Thus a *fullerene graph* is defined as a *three-regular planar* graph with only pentagonal and hexagonal faces. Moreover, fullerene graphs are the planar projection of the Platonic and Archimedean Solids.

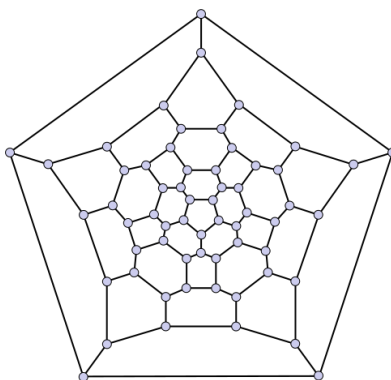


Figure 1: Buckminsterfullerene Graph

1.3 Euler's Formula (Graph Theory)

A *planar* graph is one that can be drawn in the plane with no edge crossings. One of Leonhard Euler's (1707-1783) primary contributions to mathematics, (referred to simply as *Euler's Formula*), states that for *any* planar graph the following equation must hold:

$$|v| - |e| + |f| = 2$$

Where $|^*|$ represents the number of vertices (v), edges (e), and faces (f). Using Euler's Formula we can derive several identities regarding Fullerene Graphs. Since the faces of the graph are only pentagons or hexagons we know there are precisely 5 vertices per pentagon and 6 vertices per hexagon. If we call the number of pentagonal faces p and the number of hexagonal faces h we can deduce that $|v| = 5p + 6h$. However this formula is incorrect as vertices in the graph lie in more than one face thus we are over-counting. Using the fact that the graph is 3-regular we can deduce that each vertex is in exactly three faces. As such we must divide our equation by a factor of three. Thus:

$$|v| = \frac{5p + 6h}{3}$$

A similar argument will get us the formula for the number of edges $|e|$. The naive solution to the number of edges would be $|e| = 5p + 6h$ as each pentagonal face would have 5 edges and each hexagonal 6. However since the

edges separate the faces each edge will be in two faces. Therefore we must divide by a factor of 2:

$$|e| = \frac{5p + 6h}{2}$$

Trivially the number of faces is:

$$|f| = p + h$$

Putting all of these formulas into Euler's Formula we get:

$$\frac{5p + 6h}{3} - \frac{5p + 6h}{2} + p + h = 2$$

Performing basic arithmetic this becomes:

$$\frac{10p}{6} + 2h - \frac{15p}{6} - 3h + \frac{6p}{6} + h = 2$$

Combing like terms we see that h cancels out of the equation and the terms involving p simplify to:

$$\frac{p}{6} = 2$$

From this we can deduce that for *any* fullerene graph there are *exactly* 12 pentagonal faces. This is quite a powerful result as theoretically we could choose a graph with a trillion vertices. Graphically this may be difficult to picture however chemically there is no physical limit to the number of atoms a given molecule could have. Using the fact that $p = 12$ we can also deduce other characteristics of fullerenes that are not immediately apparent. For instance, replacing p with 12 to our formula for number of vertices we see that:

$$|v| = \frac{5 * 12 + 6h}{3} = 20 + 2h$$

Therefore the smallest possible fullerene graph/molecule would be the result of choosing $h = 0$. This graph would consist of only pentagonal faces and would have 20 vertices. This graph is known as the dodecahedral graph, as it is the planar projection of the dodecahedron. The graph corresponds to the C_{20} molecule given by Figure 2. Choosing different values for h will generate all the different fullerene graphs with one particular exception.

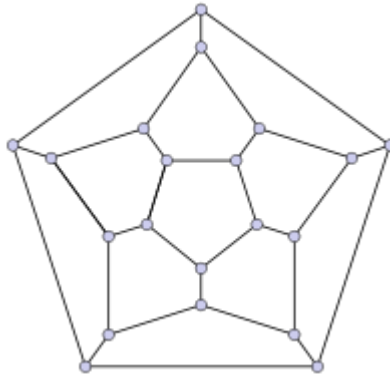


Figure 2: Dodecahedral Graph

1.4 The 22-Fullerene Problem

If we choose $h = 1$, we would generate a fullerene graph with 22 vertices, 12 pentagonal faces and 1 hexagonal face. Plugging in these values into Euler's Formula we get:

$$22 - \frac{5 * 12 + 6}{2} + 12 + 1 = 2;$$

thus

$$22 - 33 + 13 = -11 + 13 = 2$$

Thus Euler's Formula holds. To construct this graph we would first start with the dodecahedral graph and insert a hexagon into the middle: Examining this graph we see that by inserting the hexagon in the middle it forces the outer face to become a hexagon in order to preserve 3-regularity as given by Figure 3. A rigorous proof of the nonexistence of the 22-fullerene is provided by Grunbaum and Motzkin (1963). They were also able to prove the nonexistence of fullerenes on 62, 64, 66, and 68 vertices. These graphs would correspond to choosing 21, 22, 23, and 24 hexagons respectively. Aside from these counterexamples, any even value of vertices greater than or equal to 20 holds. The chemical implications of this is that a molecule with 22, 62, 64, 66, or 68 vertices would not have the fullerene structure.

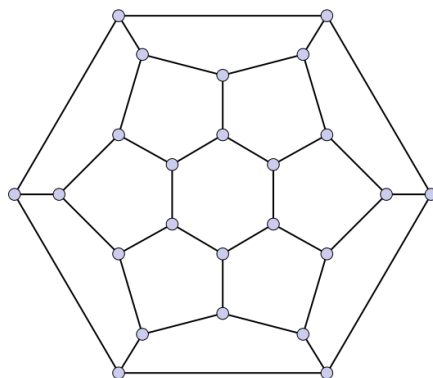


Figure 3: A failed Attempt to Construct the 22-Fullerene

2 Combinatorial 2-D Zeolites

2.1 Basic Definition

A *combinatorial d -dimensional zeolite* is a connected complex of corner sharing *simplices*. For this masters project we will only consider simplices that are equilateral triangles. If we consider every corner of the triangles as a vertex we will have two triangles at every vertex. A toy example of a zeolite is given by figure 4. The only vertices that don't have two triangles are the two top corners as well as the two bottom corners however wrapping this around it self would satisfy that condition.

2.2 Generating Zeolites via Line Graphs

To generate different zeolites we make use of the *line graph*. To generate the line graph of a graph we take each edge of the graph and make it a vertex in the line graph. Vertices in the line graph are connected if their corresponding edges share a vertex in the original graph. In order to generate a line graph with triangular faces we will require that the original graph be 3-regular.

2.2.1 K_4

A basic example of a graph and its line graph is given by Figure 5. The original graph (the complete graph on 4 vertices, referred to as K_4) has 6

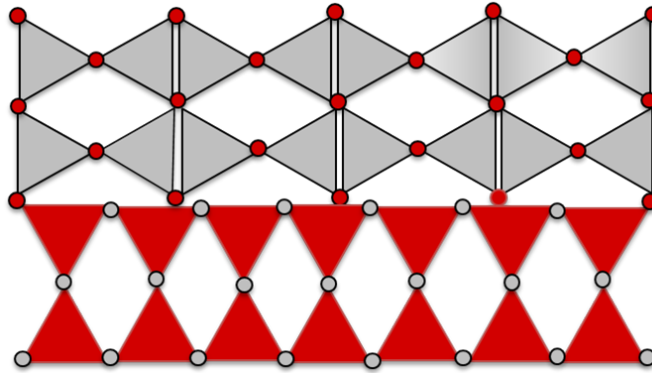


Figure 4: A section of a zeolite chain

edges, therefore its line graph has 6 vertices. Looking at the line graph of

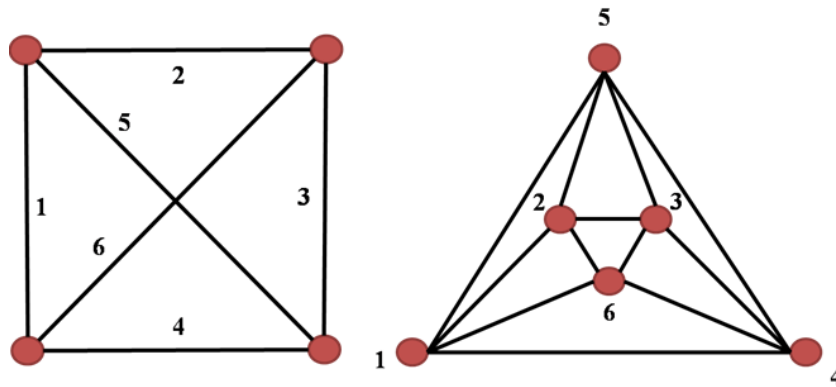


Figure 5: Complete Graph on four vertices and its line graph

K_4 we can see the zeolite structure as all of the faces are triangles. However at every vertex we have more than two triangles. In fact at vertex 6 we have four triangles. We must now differentiate between triangular faces and triangular *holes* in each line graph. We can see that if we define our triangles as in Figure 6, then naturally the triangles 126, 346, 235 are triangular holes in the graph.

$$\begin{array}{l}
1: \begin{cases} \Delta 125 \\ \Delta 164 \end{cases} \quad 4: \begin{cases} \Delta 164 \\ \Delta 345 \end{cases} \\
2: \begin{cases} \Delta 125 \\ \Delta 236 \end{cases} \quad 5: \begin{cases} \Delta 125 \\ \Delta 345 \end{cases} \\
3: \begin{cases} \Delta 236 \\ \Delta 345 \end{cases} \quad 6: \begin{cases} \Delta 164 \\ \Delta 236 \end{cases}
\end{array}$$

Figure 6: Triangles of the K_4 line graph

2.2.2 Graph of the Cube

We now perform the same transformation on the graph of cube as shown in Figure 7. Figure 8 shows the triangles in this graph which at first glance are much more difficult to distinguish.

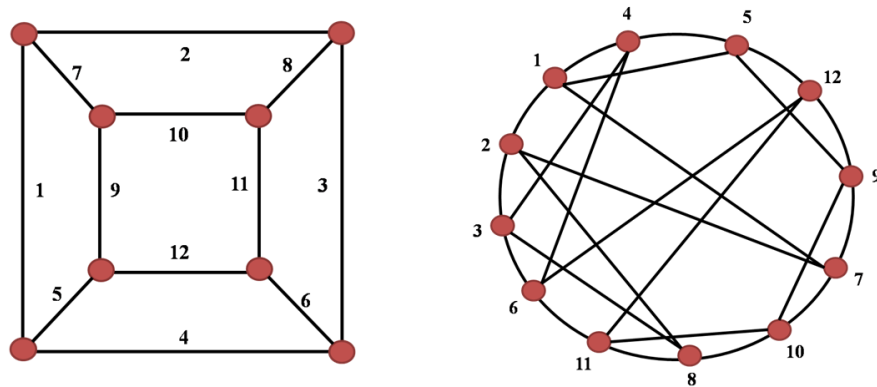


Figure 7: Cube Graph (left) and its line graph (right)

$$\begin{array}{l}
1: \begin{bmatrix} \Delta 1 & 2 & 7 \\ \Delta 1 & 4 & 5 \end{bmatrix} \quad 4: \begin{bmatrix} \Delta 1 & 4 & 5 \\ \Delta 3 & 4 & 6 \end{bmatrix} \quad 7: \begin{bmatrix} \Delta 1 & 2 & 7 \\ \Delta 7 & 9 & 10 \end{bmatrix} \quad 10: \begin{bmatrix} \Delta 7 & 9 & 10 \\ \Delta 8 & 10 & 11 \end{bmatrix} \\
2: \begin{bmatrix} \Delta 1 & 2 & 7 \\ \Delta 2 & 3 & 8 \end{bmatrix} \quad 5: \begin{bmatrix} \Delta 1 & 4 & 5 \\ \Delta 5 & 9 & 12 \end{bmatrix} \quad 8: \begin{bmatrix} \Delta 2 & 3 & 8 \\ \Delta 8 & 10 & 11 \end{bmatrix} \quad 11: \begin{bmatrix} \Delta 6 & 11 & 12 \\ \Delta 8 & 10 & 11 \end{bmatrix} \\
3: \begin{bmatrix} \Delta 2 & 3 & 8 \\ \Delta 3 & 4 & 6 \end{bmatrix} \quad 6: \begin{bmatrix} \Delta 3 & 4 & 6 \\ \Delta 6 & 11 & 12 \end{bmatrix} \quad 9: \begin{bmatrix} \Delta 7 & 9 & 10 \\ \Delta 5 & 9 & 12 \end{bmatrix} \quad 12: \begin{bmatrix} \Delta 5 & 9 & 12 \\ \Delta 6 & 11 & 12 \end{bmatrix}
\end{array}$$

Figure 8: Triangles of the Cube line graph

2.2.3 Non-Planar $K_{3,3}$

Lastly we consider a non-planar example. Figure 9 represents the non-planar bipartite graph $K_{3,3}$ and its line graph.

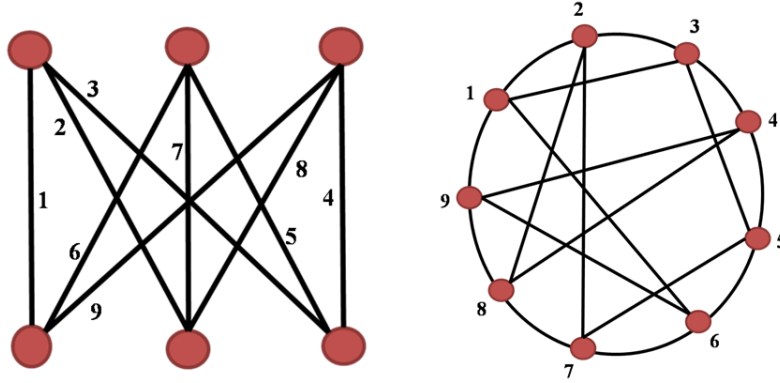


Figure 9: $K_{3,3}$ (left) and its line graph (right)

$$\begin{array}{l}
1: \begin{bmatrix} \Delta 1 & 2 & 3 \\ \Delta 1 & 6 & 9 \end{bmatrix} \quad 4: \begin{bmatrix} \Delta 3 & 4 & 5 \\ \Delta 4 & 8 & 9 \end{bmatrix} \quad 7: \begin{bmatrix} \Delta 2 & 7 & 8 \\ \Delta 5 & 6 & 7 \end{bmatrix} \\
2: \begin{bmatrix} \Delta 1 & 2 & 3 \\ \Delta 2 & 7 & 8 \end{bmatrix} \quad 5: \begin{bmatrix} \Delta 3 & 4 & 5 \\ \Delta 5 & 6 & 7 \end{bmatrix} \quad 8: \begin{bmatrix} \Delta 2 & 7 & 8 \\ \Delta 4 & 8 & 9 \end{bmatrix} \\
3: \begin{bmatrix} \Delta 1 & 2 & 3 \\ \Delta 3 & 4 & 5 \end{bmatrix} \quad 6: \begin{bmatrix} \Delta 1 & 6 & 9 \\ \Delta 5 & 6 & 7 \end{bmatrix} \quad 9: \begin{bmatrix} \Delta 1 & 6 & 9 \\ \Delta 4 & 8 & 9 \end{bmatrix}
\end{array}$$

Figure 10: Triangles of $K_{3,3}$ Line Graph

2.2.4 Conclusions

An interesting observation from these line graphs is the existence of two distinct *Hamiltonian Cycles*. A *Hamiltonian Cycle* is a path where each vertex crossed exactly once. From the line graphs we can see the first Hamiltonian cycle by tracing a path around all the vertices. The second is achieved by doing the same procedure through all the vertices using the edges in the interior of the graph. For the K_4 line graph we have cycles (1 2 6 3 4 5) and (1 4 3 5 2 6). For the line graph of the cube graph we have cycles (1 4 5 12 9 7 10 8 11 6 3 2) and (1 5 9 10 11 12 6 4 3 8 2 7). Lastly for the $K_{3,3}$ line graph we have cycles (1 2 3 4 5 6 7 8 9) and (1 3 5 7 2 8 4 9 6). From this we can theorize that 2-D zeolites (ie line graphs of 3-regular graphs) are the edge-disjoint union of two Hamiltonian Cycles.

2.3 Grünbaum Example

2.3.1 Introduction

In a 1988 paper entitled *Structural Topology*, Branko Grünbaum claims that the smallest arrangement of non-overlapping triangles such that at every vertex there are exactly two triangles has 42 triangles as given in Figure 11. We notice that the structure can be partitioned into equivalent thirds as seen by the figure on the right. Examining the partition we see that there is a total of 14 triangles (excluding the additional four on the far right). If

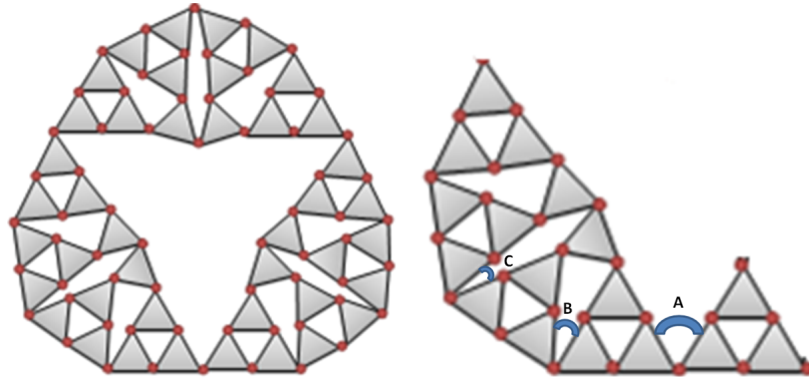


Figure 11: Grünbaum Example (left) with partition on right

we take each set of four triangles as one unit we see that the Grünbaum Example has twelve of these units. Therefore we can conclude that the outer shell of the Grünbaum Example is a dodecagon. Basic geometry tells us that the sum of the interior angles of a dodecagon must add up to 1800 degrees or 10π (approximately 31.4159) radians. Since we know each triangle is an equilateral triangle, we know that at each angle of the dodecagon we must add 120 degrees (2.0944 radians). Since there are 12 of these angles we must add a total of 1440 degrees (25.1327 radians). Subtracting this from 31.4159 we get 6.2832 radians. With these angles taken care of all we are left with are angles of degree A, B, or C as labeled in Figure 11. From here we can arrive at the following equation:

$$3A + 6B + 3C = 6.2832$$

$$A + 2B + C = 2.0944$$

Since this system is underconstrained we must find other means to calculate two out of the three unknowns.

2.3.2 Calculating the other Angles

In order to solve for these angles we must assume that the length of any side of each triangle is 1 as well as examine the shapes of the holes (areas shaded white in Figure 11). We will also use radians as our unit of measure. The shape of the hole involving angle B we see is an isosceles triangle as given

by Figure 12. Using the law of cosines we can figure out the measure of the

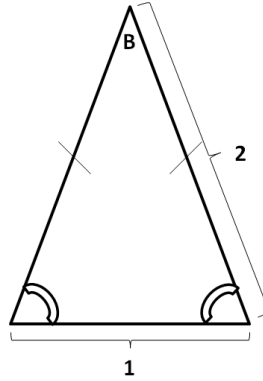


Figure 12: Isoceles Triangle Hole

angle B:

$$c^2 = a^2 + b^2 - 2ab * \cos(B)$$

thus

$$\begin{aligned} 1^2 &= 2^2 + 2^2 - 2(2 * 2) * \cos(B) \\ -7 &= -8\cos(B) \end{aligned}$$

thus

$$B = .5054$$

Although we now have the measure of B we must solve for one more of the unknowns. Since the hole including the angle A is not a known geometric shape we choose to solve for the angle C. This hole is a kite as given in Figure 13. First we must solve for the two congruent angles in the kite. To do so we subtract the measure of one of the congruent angles of the isosceles triangle plus two times the measure of one angle of the equilateral triangle from $2 * \pi$.

$$= 2\pi - (1.3181 + 2 * 1.0472) = 2.8707$$

Now that we have this angle we can compute the length of the diagonal d of the kite by splitting the kite in half and using the law of cosines.

$$d = \sqrt{1^2 + 2^2 - 2 * (1 * 2)\cos(2.8707)} = \sqrt{5 - 4\cos(2.8707)} = 2.9756$$

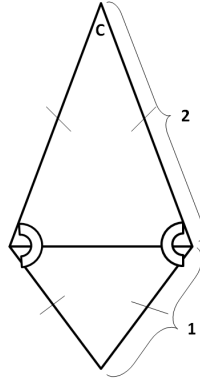


Figure 13: Kite Shaped Hole

Now that we have the length of the diagonal we solve for the length of the angle C again using the law of cosines. Since the diagonal bisects the angle C we must multiply our final answer by 2.

$$C = 2 * \arccos\left(\frac{2^2 + 2.9756^2 - 1^2}{-2 * 2 * 2.9756}\right) = 2 * \arccos\left(\frac{11.8542}{11.9024}\right) = .1801$$

Now that we have angles B and C we can find angle A using the equation generated by the fact that the construction is a dodecagon.

$$A + 2B + C = 2.9044 = A + 2(.5054) + .1801 = 2.9044, A = .9035$$

2.3.3 Rigidity

Now that we have the measure of all interior angles of the Grünbaum Example we can begin to discuss *rigidity*. For a structure to be *rigid* it must have no degrees of freedom. In context to this problem it means we cannot adjust the angles A, B, or C without violating having exactly two triangles at every vertex or disconnecting the graph. To prove whether or not this construction is rigid we again look at a section as in Figure 11. Adjusting the angle A will in turn adjust all of the angles of the holes of the graph. So first we decrease A by .01 radians. In doing so we increase B by .01 radians. If the structure is rigid, this will cause the triangles to overlap or disconnect. Now computing the measure of the congruent angles in the isoceles triangle using

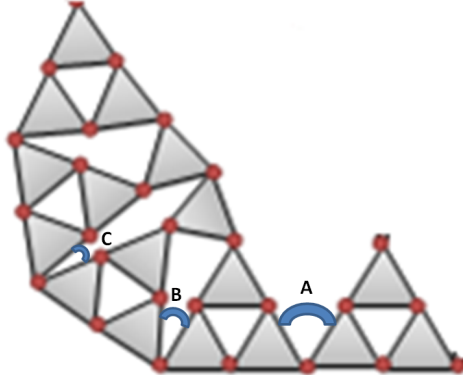


Figure 14: A section of the Grünbaum Example

law of sines we get

$$\frac{\sin(.5154)}{1} = \frac{\sin(I)}{2}$$

thus

$$I = \arcsin(2 * \sin(.5154)) = .9858$$

Using this we can solve for the congruent angle in the kite

$$K = 2\pi - (1.8088 + 1.4019) = 2.7869$$

Now we compute the length of the diagonal of the kite using the law of cosines

$$d = \sqrt{1^2 + 2^2 - 2 * (2 * 1)\cos(2.7869)} = 2.9582$$

Now using the law of sines we calculate the new measure of the angle C

$$\frac{\sin(2.7869)}{2.9582} = \frac{\sin(C)}{2}$$

thus

$$C = 2 * \arcsin(2 * \sin(2.7869)) = .4740$$

We calculate the congruent angles of this new isosceles triangle by taking $2\pi - 2.9044 - 2.7869 = 1.4019$. For this to be a triangle its interior angles must

sum to π . Therefore, $2 * 1.4019 + .4740$ should be equal to π however

$$2 * 1.4019 + .4740 = 3.2778$$

which is not equal to π . Therefore we can conclude that the Grünbaum Example is in fact rigid as increasing/decreasing any angle causes one of the vertices to break and thus make the graph disconnected or overlap thus violating our requirement that there be exactly two triangles at every vertex.

2.3.4 Minimization

Grünbaum states that his example is the smallest such arrangement of non-overlapping equilateral triangles. Taking a section of the construction as in Figure 14 we see that this alone (14 triangles) would not satisfy having two triangles at every vertex. Moreover we cannot wrap this around itself to make a quadrilateral because the interior angles of this quadrilateral would be greater than 8.3776 radians, far greater than the required 2π radians. If we doubled the section (28 triangles) as given in Figure 15, we would need d_1 to be greater than d_2 to prevent overlap. Clearly d_1 is not greater than

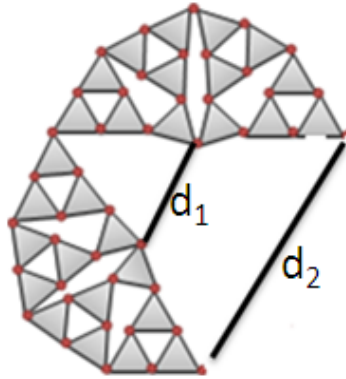


Figure 15: A section of the Grünbaum Example

d_2 and thus such a construction is impossible. Adding one more section of 14 triangles gives us the Grünbaum Example. From 42 on we can construct new zeolites by replacing every triangle with the set of triangles given in Figure 16. Since we are doing this 42 times, we can generate a formula for

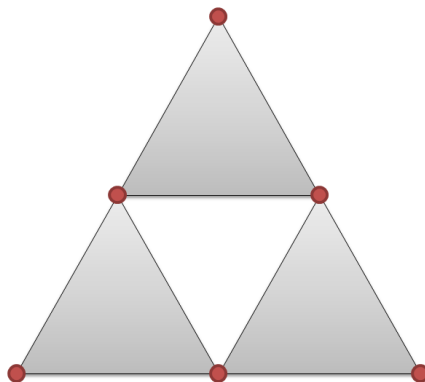


Figure 16: New unit triangle

the number of triangles for each new construction.

$$Triangles = 3^n * 42; n = 0, 1, 2, \dots$$

2.4 Harborth Example

Grünbaum's formula does not include all possible constructions. In fact all we have to do is add sections of 14 triangles to Grünbaum's example to generate more zeolites. These are documented in a 1990 paper by Heiko Harborth entitled *Plane four-regular graphs with vertex-to-vertex unit triangles*. In addition to the 42 triangle construction, Harborth introduces the next smallest construction which simply adds another section of 14 triangles as given by Figure 17. We can use the same argument as the previous example to prove rigidity. Moreover we simply add more sections of 14 triangles to generate larger constructions. From this we can conclude that all examples of this nature must have a common factor of 14.

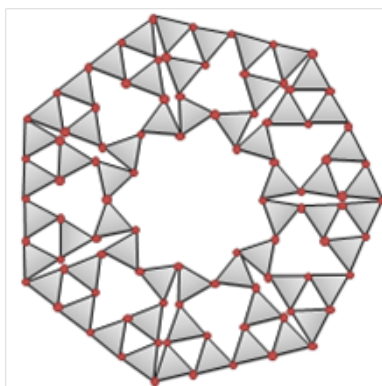


Figure 17: Harborth Example

3 3-D Zeolites

3.1 Chemical Zeolites

Zeolites are chemical compounds that are traditionally used as microfilters as well as in commercial absorbents. At the molecular level zeolite molecules bond together in a chainlike structure where each molecule is a tetrahedral molecule as given in Figure 18. The molecule SiO_4 as given in Figure 18 is a tetrahedral molecule as the four oxygen atoms repel each other due to intermolecular forces as well as carrying the same charge. Since Oxygen has

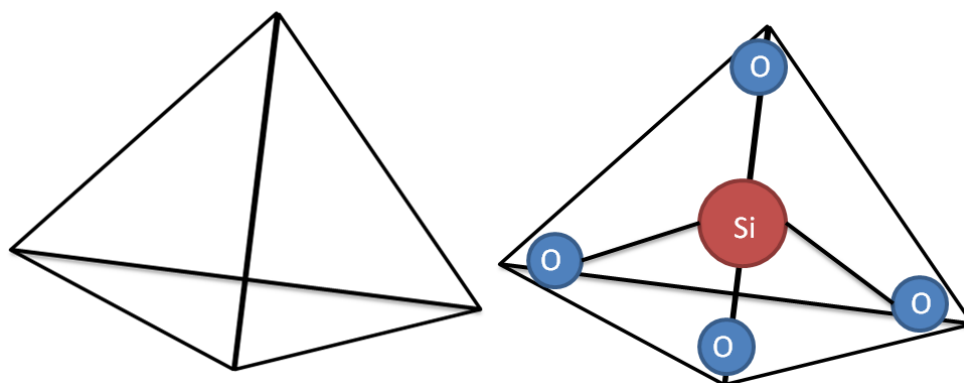


Figure 18: Tetrahedron (left) and Tetrahedral Molecule (right)

6 valence electron it requires two to be bonded in order to satisfy having eight valence electrons for every atom of the molecule. Therefore one electron of each Oxygen atom is bonded to the central Silicon atom. Since we still have that extra valence electron each tetrahedral molecule must bond to another tetrahedral molecule forming a chainlike structure. Therefore we can classify the molecular structure of SiO_4 as a 3-D zeolite with unit tetrahedra.

3.2 A Mathematical Approach

If we consider the molecular structure of compounds with tetrahedral molecules as a lattice of unit tetrahedra we can further understand specific properties of said molecules. This isn't too dissimilar from our 2-D examples as we simply substitute for every triangle a unit tetrahedron thus expanding into three dimensions.

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