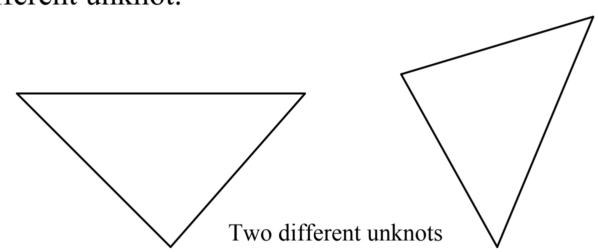
The Relation of Chemistry to Knot Theory

Originally, knot theory began as a result of a hypothesis made by Lord Kelvin that atoms were rings knotted in different ways to produce different elements. While this theory has long been disproved, mathematicians became interested in the study of knots. There are two main applications of knot theory. One is in the study of statistical and quantum mechanics. The other is the study of how to determine chirality, whether a molecule can be rigidly deformed to its mirror image, in molecules, which is what I studied. The study of chirality is important when looking at certain types of enzymes and how they interact, as well as in the study of DNA.

A knot is a simple closed polygonal curve in $\mathbb{R}^3$. The trivial knot, or *unknot*, is the knot determined by three noncollinear points. Two different sets of three points each will yield a different unknot.

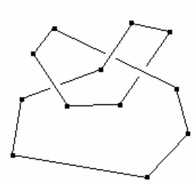


Two different unknots

The study of equivalence between knots then becomes important. In order to study the properties of knots in depth, we need a way to draw them that does not require three dimensions. The first step to determining equivalence is to define what a *regular projection* of a knot is. The function that takes the point (x, y, z) in $\mathbb{R}^3$ to (x, y) in $\mathbb{R}^2$ is called the projection map. A projection is a regular projection if no three points on the knot project to the same point, and no vertex projects to the same point as any other point on the knot.

The problem with projections is that they do not show over and under crossings. A drawing that shows the crossings in a knot is called a diagram. The over and under crossings are shown by gaps. Here is a diagram of the trefoil knot.

While a knot is usually thought of as curved, to show equivalence, it is useful to think of knots as being composed of line segments.



The trefoil knot composed by line segments

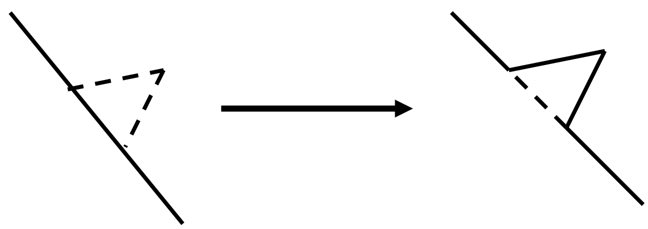
Here are several useful definitions to help us define equivalence.

Definition 1: A knot J is called an elementary deformation of the knot K if one of the two knots is determined by a sequence of points (p_1, p_2, … , p_n) and the other is determined by the sequence (p_0, p_1, p_2, … , p_n), where

(1) p_0 is a point which is not collinear with p_1 and p_n, and

(2) the triangle spanned by (p_0, p_1, p_n) intersects the knot determined by (p_1, p_2, … , p_n) only in the segment [p_1, p_n].

Here's an example of an elementary deformation:

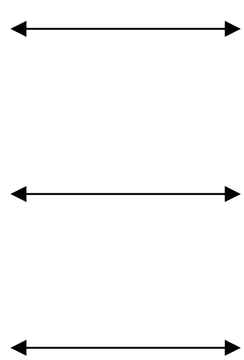


This leads us to a first definition of equivalence.

Definition 2: Knots K and J are *equivalent* if there is a sequence of knots $K=K_0, K_1,\ldots, K_n = J$, with each K_{i+1} an elementary deformation of K_i for *i* greater than 0.

Knot diagrams and projections also come in handy when showing equivalence. If two knots K and J have regular projections and identical diagrams, then they are equivalent. Knots become more useful when they are given an orientation. Equivalence is determined in the same way for oriented knots as unoriented, but it is important to pay attention to the orientation.

There are several kinds of deformations that relate knots to each other. These deformations, illustrated below are called Reidemeister moves. If two knots are equivalent, then their diagrams are related by a sequence of Reidemeister moves.



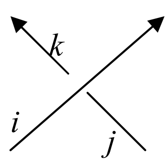
Studying the equivalence of knots led to a desire to come up with a mathematical description of knots, and an easier way to determine equivalence. So matrices were introduced into the world of knot theory. If you have a diagram of a knot, you can label each arc of the diagram with a variable x_i. Then define the relation between the variables at each crossing by $2x_i - x_j - x_k = 0 \pmod{p}$ where arc x_i crosses over arcs x_j and x_k. A knot can be labeled mod p if there is a mod p solution to the resulting system of equations with not all x_i equal. Here is an example using the trefoil knot.

The corresponding matrix will be:

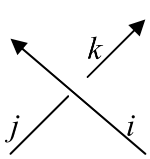
$$\begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix}$$

Continuing to study knots and their matrices led to the discovery of a polynomial to describe knots, called the Alexander Polynomial. A new way of labeling knots was developed. First, you must pick an oriented knot diagram (a diagram with direction). We'll use the oriented trefoil knot. Next, number the arcs of the diagram, and the crossings separately. To define an n x n matrix, where n is the number of crossings in the knot diagram, use the following steps:

1. If the crossing numbered l is right-handed with arc i passing over arcs j and k, as shown below, place a $1-t$ in column i of row l, enter a -1 in column j of the row, and enter a t in column k of the row.



2. If the crossing is left-handed, as shown below, enter a $1-t$ in column i of row l, enter a t in column j and enter -1 in column k of row l. Any remaining entries of row l are 0.



Next, remove the last row and the last column from the n x n matrix just defined. This (n-1) x (n-1) matrix is called the Alexander matrix of the knot. The determinant of the Alexander matrix is called the Alexander polynomial. Here is a brief example using the trefoil knot.

An oriented trefoil knot with all arcs and crossings labeled.

The matrix associated with this diagram is:

$$\begin{pmatrix} \mathbf{1-t} & \mathbf{-1} & \mathbf{t} \\ \mathbf{t} & \mathbf{1-t} & \mathbf{-1} \\ \mathbf{-1} & \mathbf{t} & \mathbf{1-t} \end{pmatrix}$$

Removing the last row and the last column yields:

$$\begin{pmatrix} \mathbf{1-t} & \mathbf{-1} \\ \mathbf{t} & \mathbf{1-t} \end{pmatrix}$$

The determinant of this matrix is $t^2 - t + 1$, which is the Alexander Polynomial for this trefoil knot. The Alexander polynomial is helpful, but is dependent on the choice of diagram you make. For example, another Alexander polynomial you can get for a trefoil knot is $-t^4 + t^3 - t^2$. If the Alexander polynomial is computed using different sets of diagrams and labelings, the two polynomials calculated will differ by a multiple of $\pm t^k$, for some integer k.

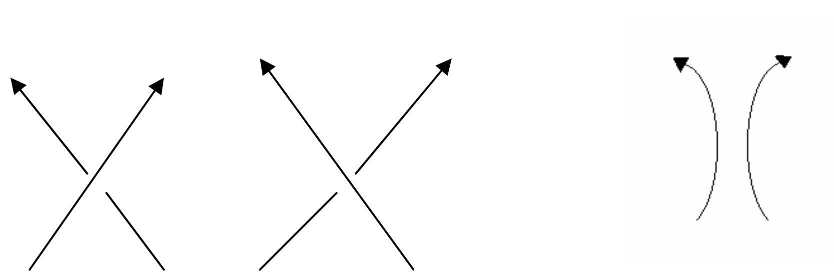
Before proceeding with our discussion of knot invariants, it is important to define a close relative of the knot, the link. A link is a finite union of disjoint knots. The *unlink* is the union of all unknots lying in a plane. In other words, a knot is a link with one component.

While the Alexander polynomial is limited in how much it tells us about knots, the study of this polynomial led to the discovery of new knot invariants that are more useful. One of the most important knot invariants is the HOMFLY polynomial, named after Hoste, Ocneanu, Millett, Freyd, Lickorish, and Yetter, its discoverers. The recursion relation for the HOMFLY polynomial is:

$$l\mathrm{P}_{L+}(l,m) + l^{-1}\mathrm{P}_{L-}(l,m) = -m\mathrm{P}_{Ls}(l,m)$$

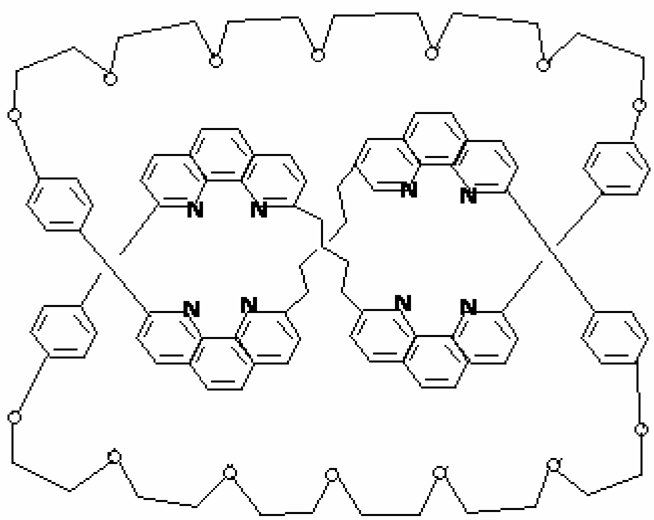
For the unknot U, $\mathrm{P}_U(l,m) = 1$.

The unlink of two components has polynomial $\mu = -m^{-1}(l+l^{-1})$. The unlink of n components has polynomial μ^{n-1}. The best way to show how to compute the HOMFLY polynomial is through an example. First, we must differentiate between L_+, L_-, and L_s. They are all identical, except at one crossing, where the difference is noted in the diagram.



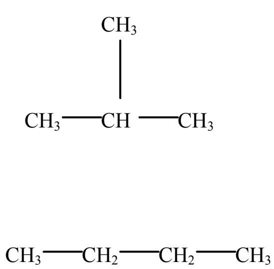
L_+ L_- L_s

All of this leads us to the study of chirality, determining whether a molecule can be deformed into its mirror image. Certain molecules, especially those in DNA and other enzymes react differently if they are chiral, meaning they cannot be deformed into their mirror image. Knot theory can be useful in determining the chirality of certain molecules since there are some molecules that are knotted.

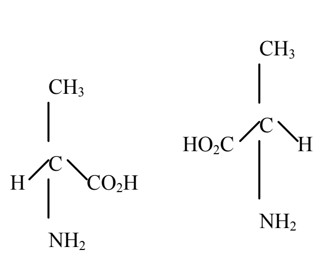


Molecular trefoil knot

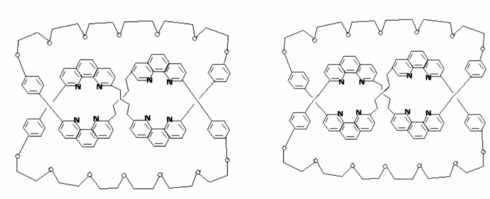
To start, we will look at isomers, the molecules structurally related to a given molecule. There are three types of isomers. Structural isomers of a molecule are the molecules that have the same molecular structure but have different molecular bond graphs. Rigid stereoisomers of a molecule are the molecules that have the same abstract graph as the given molecule but cannot be rigidly superimposed on each other. Topological stereoisomers of a molecule are the molecules that have the same abstract graph as the original molecule, cannot be deformed into each other as embedded graphs.



structural isomers



rigid stereoisomers



topological stereoisomers

The goal of using knot theory to study chirality is to find a method of determining topological chirality, which will in turn help to determine chemical chirality. First let's start with a definition of what it means for a graph to be topologically chiral, or achiral.

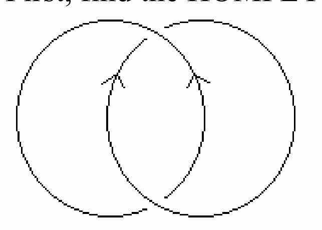
Definition: A graph embedded in three-dimensional space is topologically achiral if it can be deformed into its mirror image. Otherwise it is topologically chiral.

One of the ways to determine the chirality of a knotted molecule is by using the HOMFLY polynomial. First, we'll start with the theorem, then I'll show an example.

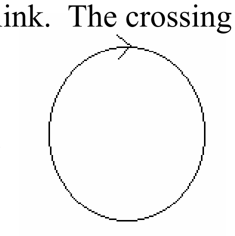
Theorem: Let $P(l,m)$ be the HOMFLY polynomial of an oriented link L. Let $P(l^{-1},m)$ be the polynomial obtained from $P(l,m)$ by interchanging l and l^{-1}. If $P(l,m)\neq P(l^{-1},m)$ then L is topologically chiral as an oriented link. If L is a knot and $P(l,m)\neq P(l^{-1},m)$ then L is topologically chiral independent of the orientation of L.

Here is an example, using the oriented Hopf link.

First, find the HOMFLY polynomial of the link. The crossing we'll use is circled.

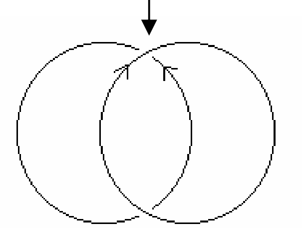


L_-



L_s

Since L_s is the unknot, $P_{Ls}(l,m) = 1$



L_+

Since L_+ is the unlink, $P_{L+}(l,m) = -m^{-1}(l+l^{-1})$

Using the recursion relation, $lP_{L+}(l,m) + l^{-1}P_{L-}(l,m) = -mP_{Ls}(l,m)$, we get

$l(-m^{-1}(l+l^{-1})) + l^{-1}P_{L-}(l,m) = -m$

Solving for $P_{L-}(l,m)$ yields $P_{L-}(l,m) = l(m^{-1}-m) + l^3m^{-1}$.

Replacing l with l^{-1} gives us $P_{L-}(l^{-1},m) = l^{-1}(m^{-1}-m) + l^{-3}m^{-1}$.

Since $P_{L-}(l,m) \neq P_{L-}(l^{-1},m)$ the oriented Hopf link is topologically chiral.

It is also possible to show that certain unoriented links are chiral using the HOMFLY polynomial. It's more difficult, and can best be shown by example. For this example, we'll look at the (6,2)-torus link.

Start by letting L be an unoriented (6,2)-torus link.

Let L’ be the oriented (6,2)-torus link from L.

Let L^* be the unoriented mirror image of L.

Use two different orientations on L^* to obtain L_1 and L_2.

If this link is topologically achiral, then $P_{L'}(l,m)$ will be equal to one of $P_{L_1}(l,m)$ or $P_{L_2}(l,m)$. By using the same method as in the previous example, we find that
$P_{L'}(l,m) = 5m^3l^{-5} + m^3l^{-7} - m^5l^{-5} - 6ml^{-5} - 3ml^{-7} + m^{-1}l^{-5} + m^{-1}l^{-7}$ and
$P_{L_1}(l,m) = -3ml^7 - 6ml^5 + m^3l^7 - m^5l^5 + 5m^3l^5 + m^{-1}l^7 + m^{-1}l^5$ and
$P_{L_2}(l,m) = m^{-1}l^{-5} + ml^{-3} + m^{-1}l^{-7} - ml^{-5} - ml^{-1}$.

Obviously, $P_{L'}(l,m) \neq P_{L_1}(l,m)$ and $P_{L'}(l,m) \neq P_{L_2}(l,m)$, so the (6,2)-torus link is topologically chiral as an unoriented link.

It’s important to note that if a molecule is topologically chiral, it is chemically chiral. However, a molecule can be topologically achiral, yet chemically chiral since some molecules are more rigid than our knot diagrams.

Continuing to see how knot theory relates to chemistry, we will now look briefly at DNA. The basic structure of DNA consists of two molecular strands twisted together in a right-handed helix. It is composed of sugars and phosphates, with each sugar having one of four bases attached to it. Bases come in pairs, adenine (A) with thymine (T), and cytosine (C) with guanine (G). Each sugar has a site called the 3’ site and one called the 5’ site. Each phosphate is joined to the 3’ site of one sugar and the 5’ site of another. The ends of the two strands in duplex DNA consists of one 3’ site on one strand and a 5’ site on the other, at the other end of the strands, there is a 5’ site on one strand and a 3’ site on the other.

Duplex DNA can exist in both a linear form and a closed circular form. The linear form is more common than the closed circular form. Closed, circular DNA can be found in nature knotted and linked. If two strands of DNA are linked, they will have the form of a (2,*n*)-torus link. Since a (2,*n*)-torus link is topologically chiral for all $n > 1$, linked DNA is topologically chiral, and therefore is also chemically chiral. If two DNA molecules have the same sequence of base pairs, but a different linking number, then they are topological stereoisomers, and thus also chemical stereoisomers. To clarify the previous statement, the *linking number* of oriented knot projections K_1 and K_2, written $Lk(K_1,K_2)$, to be one-half of the sum of +1 for every positive crossing between K_1 and K_2 and –1 for every negative crossing between K_1 and K_2.

Sometimes DNA becomes *supercoiled*. This occurs when the DNA twists more or fewer times than normal. DNA in its relaxed state has one full twist for every 10.5 base pairs, so if more or fewer twists are introduced into the strand, the DNA will twist into something that looks similar to an overused telephone cord in order to minimize the torsional stress. DNA can also become supercoiled by wrapping itself around another protein molecule. When DNA is supercoiled, it takes up less space and can be stored more efficiently. Supercoiling also affects many of the biological, chemical, and physical properties of DNA. Most notable, supercoiling make recombination easier by bringing distant sites on the DNA molecule closer together. Knot theory helps to determine how compact a supercoiled DNA molecule is by examining the linking number and other invariants derived from the linking number. This is valuable to chemists and molecular biologists because the shape and compactness of the DNA molecule will affect how it interacts with enzymes and other DNA molecules.