Molecular Catenanes, Rotaxanes and Knots

A Journey Through the World of Molecular Topology

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Foreword

Almost a century has elapsed between Willstätters 'visionary' speculation about a molecule made of two interlocked rings – a catenane – and the todays outspreading molecular chemistry concerned with topology.

After the very early achievements due to the real pioneers of chemical topology who forty years ago first acceeded to that intriguing molecule that is a catenane (by statistical threading approach: Wasserman, 1960 or by a directed approach: Lüttringhaus and Schill, 1964), this peculiar field of research concerned with molecules whose prime feature rests without doubt on beauty and non trivial spacial arrangement, has in the beginning of the 80's literaly exploded with the apparition of various templated approaches.

Creative imagination led chemists to use as templates either transition metals, π donor-acceptor effects or hydrogen bondings in order to build up around a central core or by multi-fragment interactions, more and more complex molecules, from the plain [2]-catenanes to higher entwined and complex molecular edifices like knots, doubly interlocked or poly-catenanes. Step by step, with an ever increasing rate and more and more sophisticated targets, the actual achievements realized by molecular chemists today go far beyond Willstätters original early dream.

But if in the beginning such molecules were mainly perceived as synthetic challenges, they were soon connected to nature and reality with the discovery in the early 60's of catenated or knotted DNA.

Unexpectedly, this field of research, actively supported by rigorous mathematical theories, glided furtively from pure curiosity towards much more concrete and tangible domains.

After numerous answers were brought to the synthetic challenge itself, there arose ever more insistently the quest for functions and properties of such special compounds. Already, even if still far from real applications, one can imagine, based on interlocked, threaded or knotted multi-component molecules, new organic materials, specific polymers, molecular devices or machines able to process and transfer energy, electrons or information.

We hope that the present book which gathers articles from very different scientific horizons will allow the reader to gain an overview on a fascinating broad area of science and to appreciate the long way covered in only a few decades.

We would particularly like to thank each of the authors for making time in their busy schedules to contribute a chapter to this book.

Jean-Pierre Sauvage, Christiane Dietrich-Buchecker
Strasbourg, September 1998

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1 Chemical Topology – Statistical Musings

E. Wasserman

Chemical topology was undoubtedly discussed for decades before serious laboratory efforts began. When cyclic compounds were known, the imagination could play with conjectures about catenanes and knotted rings. In 1961, on a visit to V. Prelog at the ETH, he told me about a conversation with L. Ruzicka many years earlier. Ruzicka mentioned that R.M. Willstätter had discussed the possibility of interlocked rings in a talk in Zurich before 1912 [1]. The awareness of these three chemists, major contributors to our knowledge of small- and medium-sized rings ($\lesssim 30$ carbon atoms), suggests that the concept of catenated cycles had been in the air for many years.

The broad landscape of chemical topology and topoisomerism has been summarized in comprehensive reviews [2–5]. The accomplishments of Schill, Walba, Sauvage, Stoddart, and others are landmarks in organic synthesis. This chapter describes a personal odyssey in which the focus is on statistical approaches – tinged by polymer science in their continual reference to the flexibility of chains. Some early laboratory efforts, and the technical considerations which led to them, are discussed, as is more recent activity.

1.1 Catenanes

I was introduced to interlocked rings in 1956 by M.S. Newman, a seminar speaker at Harvard. In informal discussion after the talk he described the proposal of a graduate student at Ohio State, L. Friedman, for a many-step synthesis of a catenane. The final reaction was cleavage of the two bonds connecting the linked and chemically bound rings.

I was intrigued. Mulling over the problem later that evening, and considering the need both to form and to detect catenanes, a statistical approach seemed attractive. Synthesis of a C_{30} ring from a linear precursor in the presence of an inert C_{20} cyclic compound should enable threading of some of the smaller rings before cyclization. A C_{50} product would indicate the presence of an interlocked system.

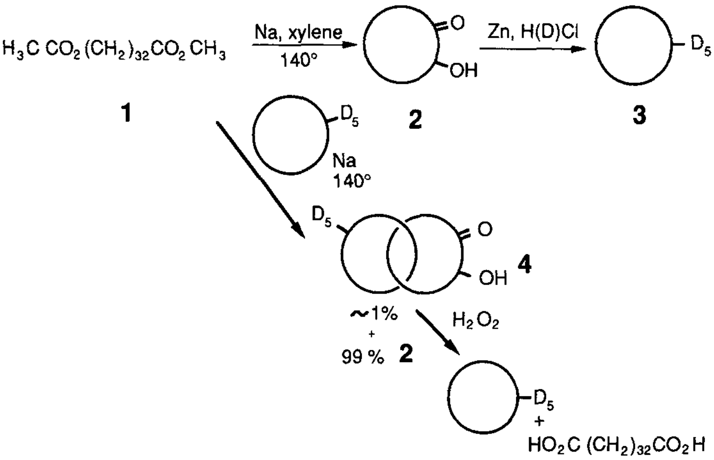


Figure 1. Experimental route to a 34,34-catenane.

At Bell Laboratories the following year, I manipulated space-filling models and found that a ring $\gtrsim C_{24}$ was required for a polymethylene chain to pass through. Larger rings were preferred as they should be more likely to have sufficiently open conformations. The acyloin condensation of an α, ω diester offered a particularly efficient route to carbocycles. With the largest reported diacid containing 34 carbon atoms, these considerations pointed to a 34,34-catenane as the goal. The experimental route is given in Figure 1 [6].

After chromatographic removal of **3**, the cleavage of the catenane, **4**, to **3** and **1** was critical evidence of the structure. Numerous blank experiments excluded other possibilities. Figure 1 essentially describes a double-labeling experiment; deuterium for one ring and the acyloin function for the other, the labels detected by their infrared absorption [6]. The few milligrams of purified **3** could not be crystallized. The name 'catenane' was based on the Latin 'catena' for 'chain'.

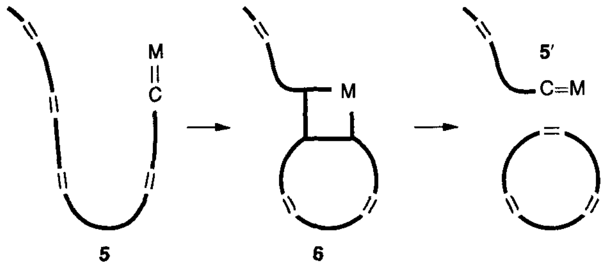
The stability of the catenated link under laboratory conditions, e.g. chromatography, is essentially demonstrated in Figure 1. Simple calculations of the probability of tunneling of one C-C bond through another gave unobservably small values. Although expected, the evidence for the robust structure was reassuring.

More information on threading was reported by Harrison and Harrison in some elegant studies. They demonstrated that a polymethylene could thread a C_{30} ring bound to a Merrifield resin to form a hooplane or rotaxane when the ends were capped [7]. Using a mixture of rings alkane chains were found to thread C_{24} and larger cycles with a probability which increased with ring size. Values of ~1% were found near C_{30} [8]. The low probability of threading [6, 7] made the formation of multiply-threaded polymeric systems unlikely [9–11]. Attempts at synthesis were made by Lüttringhaus et al. [12] and by Lemal [13]. They constructed systems in which the closure of a second ring would have led to catenanes in high yield.

1.2 Olefin Metathesis

Another route to catenated structures became possible via the olefin metathesis reaction of Calderon et al. [14, 15]. With cyclododecene, oligomers up to C_{192} could be identified by mass spectrometry [16]. The original suggested mechanism involved a transient metal-complexed cyclobutane [14, 15]. With oligomers arising from repeated metathesis, twisting of the intermediate rings and another metathesis defines a Möbius-strip approach to catenated and knotted rings [17]. The mass spectral evidence [17] was consistent with catenanes.

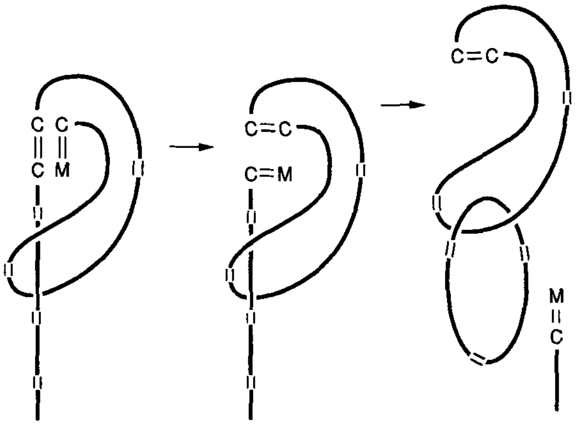
Shortly after these reports, mechanistic studies by Grubbs [18] established that metal-carbenes **5** and metalocyclobutane **6** are the critical intermediates, as shown in Scheme 1.



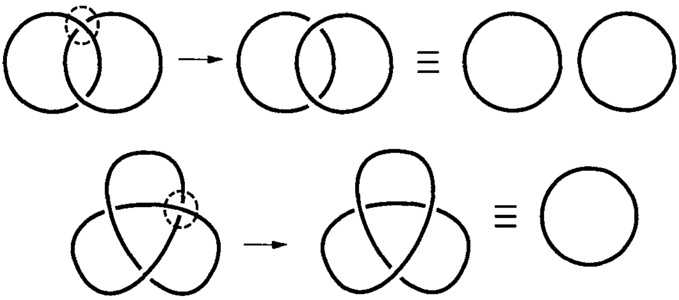
Scheme 1

This route provides access to catenanes (and knotted rings) without having to thread closed cycles, sharing an important feature of the Möbius path. The more complex ring structures arise from the tangling motions of the pendant chain before formation of the four-membered ring **6** (Scheme 2).

More generally, the metathesis reaction provides a laboratory analog of an important theorem in topology. Any linked or knotted structure can be converted to simple cycles (unknots) by selective interconversion of overcrossings and under-



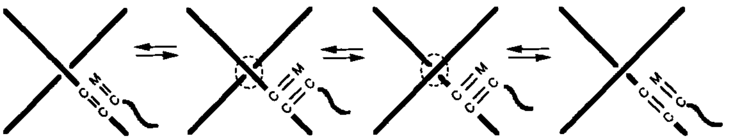
Scheme 2



Scheme 3

crossings – Scheme 3 [18]. Conversely, unknots of adequate size can be converted into any other linked or knotted species.

The metalocarbene, containing one carbon of a potential double bond, is a catalyst for the reversible breaking of an olefinic bond. Once broken the conversion of an overcrossing to an undercrossing is a change of conformation. Reforming the bond can freeze this new arrangement – Scheme 4.



Scheme 4

The mass spectra [17] give a grossly simplified picture of the complex mixture which can result from a ring-opening polymerization. Knotted isomers can have almost identical mass spectra, dominated by the parent ion. With the reversibility of metathesis, the polyolefin mixture near equilibrium is expected to contain a large variety of knotted and linked species.

A molecular biology analog of Scheme 4 is the ability of topoisomerases to interchange different knots in DNA [19].

1.3 Knots

In reference 1 we noted that a cycloalkane with >50 carbon atoms could exist as a (chiral) trefoil, and one with >72 carbon atoms as a figure-of-eight. The minimum values are for a 'tight' knot, one with little flexibility. These numbers were obtained from models and the examination was not extended to larger molecules. In the intervening years the ability to synthesize more complex systems has greatly improved. A dramatic demonstration of this progress was the directed synthesis of a trefoil by C. Dietrich-Buchecker and J.-P. Sauvage in 1989 [20].

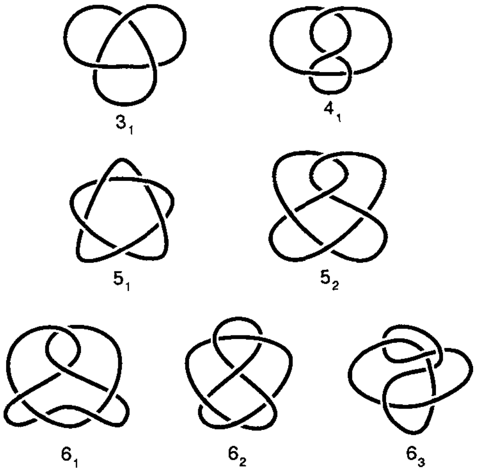


Figure 2. Threefold, fourfold, fivefold, and sixfold knots.

To examine the possibilities for knotted isomers in larger rings we note that two 5-fold knots (Figure 2) require ~83 and ~92 methylenes; the three 6-fold ~100, ~102, and ~105. Thus a C_{100} cycloalkane might exist as one of ~5 isomeric knots.

This sparse set of choices becomes richer with larger rings. With more crossings, n, the number of possible knots increases exponentially [21]. There are 21 for $n=8$, 165 for $n=10$, and 2176 for $n=12$ [22]. Models indicate that many 12-fold knots should be stable in a cycloalkane of ~C_{200}. The rapid increase in the number of possible knots between C_{100} (~5) and C_{200} (~3000) results from the dependence of allowed values of n on ring size.

One can excise ~4 carbon atoms, and the loop in the shape of a lock-washer which pivots around them, to convert an n-crossing knot into an n–2 knot. Some 30 carbon atoms are removed in this transformation. Examples would be the conversion of the 6-fold knots (Figure 2) into the figure-of-eight, removing 28, 30, or 33 carbon atoms. In general we expect the allowed n for tight knots to increase approximately linearly with the size of the ring.

There are $>10^6$ knots for $n=16$ [23] and by extrapolation there will be $>10^7$ for $n=18$. Thus a ring of ~300 carbon atoms has the potential for tens of millions of knotted isomers, most of which will be chiral. The laboratory tests of these conjectures are left as an exercise for the reader.

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Dr. L. Barash performed the Herculean labor of preparing the catenane, **3**. Drs A.M. Trozzolo and H.L. Frisch were always willing to engage in thought-provoking conversation. More recently, discussion with Professors D.W. Sumners, S.G. Whittington, and J. Simon familiarized me with recent mathematical advances relevant to chemical topology.

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2 A Knot Theoretic Approach to Molecular Chirality

Erica Flapan

This chapter will begin by explaining some topological techniques to prove that a knot, link, or embedded graph cannot be deformed to its mirror image. We shall explain how to use these topological techniques to prove that the graphs of many of the recently synthesized chemical knots and links cannot be deformed to their mirror images. Then we present an alternative approach to analyzing whether a molecular structure can be deformed to its mirror image, by using a molecular cell complex rather than a molecular graph to represent a molecule. We will present examples of molecular cell complexes, and explain how to prove that an embedded cell complex cannot be deformed to its mirror image. Finally, we give examples of chiral molecules whose molecular cell complexes cannot be deformed to their mirror images yet whose molecular graphs can be deformed to their mirror images. Thus in these examples, the topology of the molecule is more accurately represented by a molecular cell complex than by a molecular graph.

2.1 Topological Chirality of Knots and Links

Topologists became interested in chirality with the development of knot theory, which itself grew out of chemistry. In the late nineteenth century, Lord Kelvin developed the theory that atoms were vortex rings which were knotted or linked in different ways according to what element they were [1]. Motivated by this theory, Peter Guthrie Tait created tables of different knots and links with the hope of building a periodic table [2]. Tait defined a *knot* to be a simple closed curve in 3-space, and a *link* to be one or more disjoint simple closed curves in 3-space. He defined two knots or links to be topologically equivalent if one can be deformed to the other, where a deformation of a knot or link does not permit the knot or link to pass through itself. In order to provide a list of topologically distinct knots and links, Tait tried to determine whether or not each knot and link could be deformed to its mirror image.

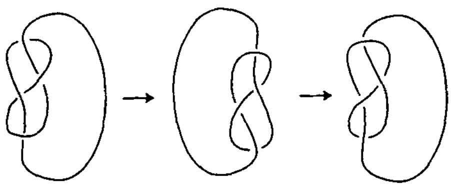

Figure 1. A deformation of a figure eight knot to its mirror image.

Ever since Tait's seminal papers on knot theory [2], topologists have been interested in which knots and links are topologically distinct from their mirror image. Nonetheless, the word 'chirality' was not used to describe knots and links until the 1980s. Prior to that time, topologists utilized Tait's terminology which defined a knot or link to be *amphichiral* if it could be deformed to its mirror image. There was no specific word to refer to a knot or a link which was not amphicheiral. As a result of the increase in communication between topologists and chemists since the early 1980s, the term *topologically achiral* is now commonly used as a synonym for amphicheiral, and knots or links which are not amphicheiral are said to be *topologically chiral.* Note that for molecular graphs the word 'achiral' can have different meanings depending on how flexible the graph is. In order to make it clear that the knots and links we are considering are completely flexible, we always speak of topological achirality rather than simply achirality.

For a knot or link which has few crossings, it may not be too difficult to see how to deform it to its mirror image. For example, Figure 1 illustrates how the figure eight knot can be deformed to its mirror image. To get from the first picture in Figure 1 to the second picture, you rotate the knot by 180° about a vertical axis. Then to get to the third picture, you flip the long string over the knotted arc without moving the knotted arc. This final picture is the mirror image of the first picture, where the mirror is in the plane of the paper. This means that the mirror has the effect of interchanging all of the overcrossings and undercrossings.

In most cases, simply examining a knot or link is not sufficient to determine whether or not it is topologically chiral. If we cannot find a deformation of it to its mirror image this does not necessarily mean that such a deformation does not exist. Perhaps if we just kept trying we would eventually find the deformation, or perhaps the knot or link is actually topologically chiral. In order to avoid this uncertainty, topologists have developed techniques to recognize when knots and links are topologically chiral. One important technique is to make use of one of the collection of link polynomials which have recently been created. We project our knot or link onto a plane in such a way that at most two points of the knot or link are projected down to the same point. Then we indicate each undercrossing by drawing a gap where one strand is meant to go under another strand. For example, Figure 1 illustrates several projections of the figure eight knot. We orient a knot by drawing an arrow to indicate in which direction we shall traverse the knot. A link is oriented by putting an arrow on every component of the link.

There are several link polynomials which are convenient to use, notably the Jones polynomial [3], the Kauffman polynomial [4], and the 2-variable HOMFLY polynomial [5]. These polynomials are all easy to explain and somewhat similar in flavor, so we present only one, the HOMFLY polynomial named after five of the authors who discovered it, Hoste, Ocneanu, Millet, Freyd, Lickorish, and Yetter. It was also independently discovered by Przytycki and Traczyk [6]. This polynomial is sometimes simply called the P-polynomial. All the link polynomials are actually Laurent polynomials, which means that the variables in the polynomials can be raised to negative as well as positive powers.

Before we define the P-polynomial we need to clarify our terminology. Recall that the word 'link' refers to one or more simple closed curves, so when it is convenient, we shall use the word 'link' to mean a knot or link. The *unknot* is defined as any simple closed curve which can be deformed into a plane, and the *unlink* is defined as any collection of one or more simple closed curves which can be deformed into the plane. We begin by fixing a particular projection of an oriented link L. The P-polynomial of L will be defined in terms of the crossings of this oriented projection. We want to distinguish two different types of oriented crossings which we will call positive crossings and negative crossings. These two types of crossings are illustrated in Figure 2. Every crossing can be rotated to look like one of the two crossings in Figure 2. Furthermore, no matter how a positive crossing is rotated, it will never become a negative crossing, and no matter how a negative crossing is rotated, it will never become a positive crossing.

Figure 2. A positive crossing and a negative crossing.

The P-polynomial is defined recursively. This means that we compute the P-polynomial of an oriented link in terms of the polynomials of simpler oriented links, which in turn are computed in terms of the polynomials of oriented links which are simpler still, and so on until we get a collection of unknots each of whose polynomial is known to equal 1.

The P-polynomial $P(L)$ has variables m and l and is formally defined from the oriented projection of L by using the following two axioms.

Axiom 1. $P(\text{unknot}) = 1$,

Axiom 2. Suppose L_+, L_-, and L_0 are oriented link projections which are identical except near a single crossing where they differ by a positive, negative, or null crossing respectively (these three possibilities are illustrated in Figure 3). Then we have $lP(L_+) + l^{-1}P(L_-) + mP(L_0) = 0$.

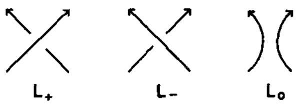

Figure 3. L_+, L_-, and L_0 are identical except at this crossing.

From its definition, the P-polynomial appears to depend on the particular projection of the link which we are working with. However, when this polynomial was defined it was proven that given any oriented link, no matter how it is deformed or projected, the link will always have the same P-polynomial [5, 6]. This means that two oriented links which are topologically equivalent have the same P-polynomial. In particular, if an oriented link can be deformed to its mirror image then it and its mirror image will have the same P-polynomial.

We illustrate how to compute the P-polynomial by evaluating a couple of examples. First let L_0 consist of the oriented unlink of two components which is illustrated in Figure 4. Then L_+ and L_- are as shown in the figure. Now we use the second axiom of the definition of the P-polynomial, together with the observation that both L_+ and L_- are topologically equivalent to the unknot, in order to obtain the equation $l + l^{-1} + mP(L_0) = 0$. Hence, we conclude that $P(L_0) = -m^{-1}(l + l^{-1})$.

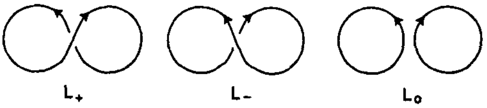

Figure 4. L_+, L_-, and L_0.

We shall use this result to enable us to compute the P-polynomial of the oriented link, illustrated as L_- in Figure 5. This link is known as the *Hopf link*. We choose the upper crossing to change so that we have L_+ and L_0 as indicated in the figure.

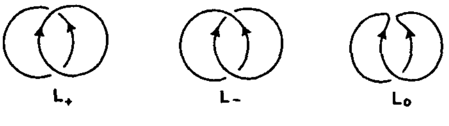

Figure 5. We compute the P-polynomial of the oriented Hopf link which is represented by L_-.

Now we see that L_0 can be deformed to the unknot and L_+ can be deformed to the link whose polynomial we computed previously. So we substitute these polynomials into the equation of Axiom 2, in order to get the equation $l(-m^{-1}(l + l^{-1})) + l^{-1}P(L_-) + m = 0$. Thus, after some simplification, we get $P(L_-) = l^3m^{-1} + lm^{-1} - lm$.

It can be seen from these simple examples that computing the P-polynomial of any complicated oriented link will be quite cumbersome. However, there are a number of excellent computer programs which will compute all of the link polynomials for any oriented link which can be drawn with up to about 50 crossings (for example, the program KNOTTHEORY by COMPUTER written by M. Ochiai, and available through anonymous ftp [7]).

Notice that the orientation of a link may affect its polynomial. For example, the Hopf link in Figure 6 has one component which is oriented in a different di-

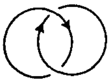

Figure 6. A Hopf link with a different orientation from that of L_- in Figure 5.

rection from the Hopf link which is illustrated as L_- in Figure 5. The P-polynomial of this new Hopf link turns out to equal $l^{-3}m^{-1} + l^{-1}m^{-1} - l^{-1}m$. The roles of l and l^{-1} in this polynomial have been reversed relative to the P-polynomial of the Hopf link illustrated as L_- in Figure 5.

In contrast with links, we can see as follows that the orientation of a knot has no effect on its polynomial. Suppose that L is a knot. Then reversing the orientation of L results in reversing all of the arrows in the diagram. In particular, it reverses the direction of both arrows occurring at any crossing. As can be seen from the positive crossing illustrated in Figure 7, a positive crossing remains positive after both arrows are reversed. Reversing the arrows simply has the effect of rotating the crossing by 180°. Similarly, negative crossings and null crossings remain unchanged by reversing all of the arrows of a diagram. Thus the P-polynomial of a knot L is independent of the orientation of the knot.

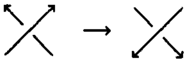

Figure 7. A positive crossing in a knot is independent of the orientation of the knot.

The link polynomials can be quite helpful if we wish to show that a specific oriented link is topologically chiral. So far we have only defined topological chirality for unoriented links. We now define an oriented link L to be *topologically achiral* if there is deformation taking the oriented link L to the mirror image of L with the corresponding orientation. An oriented link which is not topologically achiral is said to be *topologically chiral.* The theorem below, which follows from [5] and [6], tells us how to use the P-polynomial to prove that an oriented link is topologically chiral. For knots, we saw that the P-polynomial is independent of the choice of orientation. So we do not have to specify a knot's orientation in order to compute its polynomial. Thus the theorem tells us how to use the P-polynomial to prove that an unoriented knot is topologically chiral.

Theorem. *Let L be an oriented link with P-polynomial P(L). Let $\overline{P}(L)$ denote the polynomial obtained from P(L) by interchanging l and l^{-1}. If $P(L) \neq \overline{P}(L)$ then the oriented link L is topologically chiral. If K is a knot and $P(K) \neq \overline{P}(K)$ then the unoriented knot K is topologically chiral [5, 6].*

In order to see how to apply this theorem we can consider the oriented Hopf link which was illustrated in Figure 5. We determined above that the P-polynomial of this oriented Hopf link L is $P(L) = l^3m^{-1} + lm^{-1} - lm$. If we interchange l and l^{-1} we will obtain the polynomial $\overline{P}(L) = l^{-3}m^{-1} + l^{-1}m^{-1} - l^{-1}m$. Since $P(L) \neq \overline{P}(L)$, the theorem tells us that the oriented Hopf link is topologically chiral. This

Figure 8. An oriented Hopf link is topologically chiral.

means that there is no deformation which takes the Hopf link on the left side of Figure 8 to the Hopf link on the right side of Figure 8.

On the other hand, as an unoriented link the Hopf link is topologically achiral. This can be seen in Figure 9. In order to go from the first to the second picture we turn over the right hand component of the link. We can see that the second diagram is the mirror image of the first where the mirror is in the plane of the paper. However, for the oriented Hopf link of Figure 8, turning over one component would have the effect of reversing the orientation of the corresponding component of the mirror image.

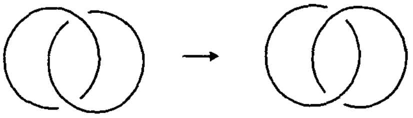

Figure 9. By turning over one component we obtain the mirror image of the unoriented Hopf link.

For knots, we can apply the theorem without having to worry about the orientations. For example, the right handed trefoil knot, which is drawn in Figure 10, has P-polynomial $P(L) = -l^{-4} + l^{-2}m^2 - 2l^{-2}$ regardless of how it is oriented. This polynomial is clearly not symmetric with respect to l and l^{-1}, so we can immediately conclude that the trefoil knot is topologically chiral. With the help of one of the computer programs to compute link polynomials, we can use the above theorem to recognize many topologically chiral knots and oriented links.

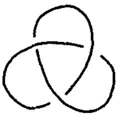

Figure 10. A trefoil knot is topologically chiral.

Note that the theorem does not detect all topologically chiral knots and oriented links, because there are topologically chiral knots and oriented links whose P-polynomials are nonetheless symmetric with respect to l and l^{-1}. For example, consider the knot which is illustrated in Figure 11. This knot is known by knot theorists as 9_{42} because this is the forty second knot with 9 crossings listed in the standard knot tables (see the tables in Rolfsen's book [9]). Using a computer program we find that the P-polynomial of the knot 9_{42} is $P(9_{42}) = (-2l^{-2} - 3 - 2l^2) + m^2(l^{-2} + 4 + l^2) - m^4$. Observe that this polynomial is symmetric with respect

Figure 11. The knot 9_{42} is topologically chiral.

to l and l^{-1}. So we cannot apply the theorem. However, using more sophisticated techniques it is possible to show that this knot is topologically chiral.

We can also use link polynomials to prove that certain unoriented links are topologically chiral. For example, let L denote the (4,2)-torus link which is illustrated on the left in Figure 12. This is called a *torus link* because it can be embedded on a torus (i.e. the surface of a doughnut) without any self-intersections. It is a (4,2)-torus link, because, when it lies on the torus, it twists four times around the torus in one direction, while wrapping two times around the torus the other way. Let L' denote the oriented link that we get by putting an arbitrary orientation on each component of the (4,2)-torus link, for example, as we have done in Figure 12. Now the P-polynomial of L' is $P(L') = -l^{-5}m^{-1} - l^{-3}m^{-1} + ml^{-5} - m^3l^{-3} + 3m\,l^{-3}$.

Figure 12. The unoriented and oriented (4,2)-torus link.

We create the link L^*, the mirror image of the unoriented link L, by switching all of the crossings of L. Since L^* has two components, there are four ways to orient L^*. Two of these orientations for L^* are illustrated as L_1 and L_2 in Figure 13. There are two additional ways of orienting L^*, however, each one of these will reverse the direction of both arrows at each crossing relative to one of the oriented links in Figure 13 and so will have the same polynomial as L_1 or L_2. We now compute the P-polynomial of each of the oriented links in Figure 13. These polynomials turn out to be $P(L_1) = -l^5m^{-1} - l^3m^{-1} + ml^5 - m^3l^3 + 3ml^3$ and $P(L_2) = -m^{-1}l^{-3} - m^{-1} - m^{-1}l^{-5} + ml^3$. We prove that the unoriented (4,2)-torus

Figure 13. We orient the link L^* in two different ways to get L_1 and L_2.

link is topologically chiral by contradiction. Suppose that the link L could be deformed to its mirror image. Hence the oriented (4,2)-torus link could be deformed to L^* with some orientation. The P-polynomial of the oriented (4,2)-torus link L' should therefore equal the P-polynomial of either L_1 or L_2. As this is not the case, we can conclude that the unoriented (4,2)-torus link is topologically chiral.

2.2 Topological Chirality of Embedded Graphs

Stimulated by the development of the interdisciplinary field of topological chemistry, topologists have extended some of the techniques from knot theory to the theory of graphs in 3-space. Graph theorists typically study graphs as abstract objects made up of vertices and edges, while topologists study graphs which have a specified position in 3-space. Such a graph is viewed as a topological object in 3-space which can be deformed but cannot pass through itself. To make it clear that we are talking about graphs in 3-space rather than abstract graphs, we refer to such graphs as *spatial graphs* or *embedded graphs*. A molecular bond graph has a configuration in space and so is an example of an embedded graph. If we add a finite number of vertices to any knot or link, we have another example of an embedded graph. By analogy with knots and links, an embedded graph is said to be *topologically achiral* if it can be deformed to its mirror image, and otherwise it is said to be *topologically chiral.*

A graph is said to be *n-valent* if every vertex of the graph has n edges coming out of it. Various results in knot theory have been extended to 3-valent and 4-valent embedded graphs. In particular, Kauffman [9] has developed a polynomial for a specific type of 4-valent embedded graphs known as rigid vertex graphs, and Yamada [10] has developed a polynomial for 3-valent embedded graphs. These polynomials are related to link polynomials and can also be used to detect topological chirality for these specific types of embedded graphs. For arbitrary embedded graphs, Kauffman also has a method of associating a collection of knots and links to the embedded graph and using these knots and links to demonstrate the topological chirality of the embedded graph [9]. We shall explain Kauffman's method in detail below.

Let G be an embedded graph. Define $T(G)$ to be the set of all knots and links which are contained in the embedded graph G. That is, $T(G)$ contains every knot and link which can be obtained by joining two edges together at each vertex and disconnecting all other edges from that vertex. Performing this operation at all of the vertices may create a number of arcs which are not closed up, but $T(G)$ does not include any of these arcs.

For example, consider the embedded graph G illustrated in Figure 14. The total collection of arcs and simple closed curves that we get by performing this operation at the vertices is illustrated in Figure 15, and the elements of the set $T(G)$ are illustrated in Figure 16.