Journal of Mathematical Chemistry 23 (1998) 31–49

Topological rubber gloves

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This paper introduces the concept of a topological rubber glove and gives several examples. In particular, we prove that the knot 8_{17} and the molecular graph of a single stranded DNA figure eight knot are topological rubber gloves. Then, we present an embedded graph which is not only a topological rubber glove, but has the additional property that no embedding of the graph can be rotated to its mirror image

Recently more and more topologically interesting molecules have been synthesized whose structure comes from their topology as well as their geometry. These new types of molecular graphs are often large enough that they no longer have the rigidity that is characteristic of small molecules. So understanding their deformations is part of understanding their symmetries. In addition to such purely synthetic molecules, molecular biologists have found that knotting and linking can occur in DNA in nature and can be manipulated in the lab. Also, Liang and Mislow [10] have discovered that knots and links can occur in proteins. So now both chemistry and molecular biology have something to gain by understanding the topology of molecular graphs in space.

For rigid structures, we know that a compound is chiral if its graph cannot be superimposed on its mirror image. However, if a molecule is completely or partially flexible, it is not so easy to determine from the graph whether or not the molecule is chiral. For such molecules, topology may be a helpful tool. The first time that topology was used to prove the chirality of flexible molecular graphs was for molecular Möbius ladders. These molecules resemble Möbius strips where the surface has been replaced by a ladder. The three rung Möbius ladders were first synthesized in 1982 by Walba et al. [19], and the four rung Möbius ladders were synthesized in 1986 by Walba et al. [18]. The sides of the three rung ladders consist of a polyether chain of 60 atoms and the rungs of the ladders are carbon–carbon double bonds.

After the first molecular Möbius ladder was synthesized, there was experimental evidence indicating that this molecule was chiral, and the molecular graph had no apparent symmetry presentation (that is, it had no presentation which could be rotated to its mirror image). However, the molecular Möbius ladders are flexible, so, in theory, such a molecule might be able to deform itself to its mirror image without ever attaining a symmetry presentation. Because of this flexibility, Walba was not able to conclude that the graph of the molecular Möbius ladder was necessarily chiral. In response to this problem, the topologist J. Simon proved that any molecular Möbius ladder with at least three rungs cannot be deformed to its mirror image [14]. In conjunction with his proof, Simon defined a molecular graph to be topologically achiral if can be deformed to its mirror image and topologically chiral otherwise. He observed that any molecule whose bond graph is topologically chiral is necessarily chemically distinct from its mirror image.

Even apart from completely flexible molecules, some molecules can interconvert with their mirror image by twisting around a specific bond or bonds. In 1954, Mislow used a biphenyl derivative to synthesize the first such molecule which could interconvert with its mirror image but whose molecular bond graph could not be superimposed on its mirror image [11,12]. The diagram of Mislow's example is given in figure 2. This molecule has vertical propellers on each end which rotate simultaneously by 90°. When the molecule rotates about a horizontal axis by 90°, and the propellers simultaneously rotate by another 90°, we obtain the mirror image of the molecule through a vertical mirror cutting across the central bond of the molecule. Apart from the simultaneous rotation of the propellers, this molecule is rigid so it can never assume a position which can simply be rotated to its mirror image. Thus Mislow's biphenyl derivative can interconvert with its mirror image, but it has no symmetry presentation.

Walba has referred to examples such as the above molecule as Euclidean rubber gloves [17]. The idea behind this terminology originally came from Van Gulick [7] in 1960, who observed that a right-handed rubber glove can be turned inside out to get a left-handed rubber glove, but at no point during the turning inside out process can the rubber glove be rigidly rotated to its mirror image. On the other hand, if the glove were flattened out, then it would lie in a plane and so it would be its own mirror image. Similarly, if we allow the graph of Mislow's molecule to become flexible it could also be flattened into a plane. But of course, on a chemical level the molecule cannot be flattened out. Walba introduced the word Euclidean to make clear that Mislow's

Figure 1. The graph of a three rung molecular Möbius ladder and its mirror image.

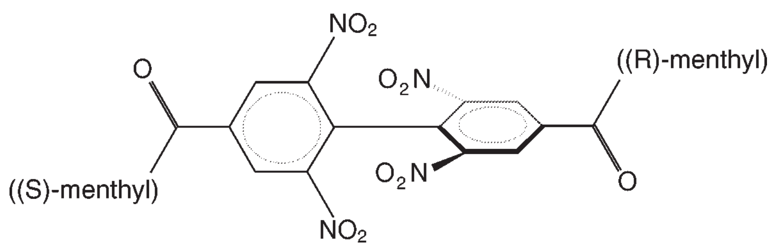


Figure 2. A molecule which can interconvert with its mirror image but cannot be rotated to its mirror image.

molecular rubber gloves actually must remain rigid apart from some bonds which can rotate.

A Euclidean rubber glove could be characterized as a molecule which is achiral, yet has no chemically accessible symmetry presentation. Walba asked whether such a structure could exist if we allow its graph to be flexible and replace the concept of chemical accessibility by topological accessibility [16]. In particular, could there exist a graph in 3-space such that if it were made flexible, then it could be deformed to its mirror image, but even if it were flexible it could not be deformed to a symmetry presentation? He called such a structure a topological rubber glove, as the flexible analog of a Euclidean rubber glove. Mislow's Euclidean rubber glove is not a topological rubber glove, since if the graph were flexible then it could be deformed into the plane, and hence would be its own mirror image.

It is not always obvious whether or not a structure has a symmetry presentation. Walba initially conjectured that the figure eight knot was a topological rubber glove since he could see how to deform it to its mirror image, but he could not find a symmetry presentation for it. Figure 3 illustrates a deformation of the figure eight knot to its mirror image. To get from the first picture 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.

At no point during the above transformation of the figure eight knot to its mirror image can the knot actually be rotated to its mirror image. However, the figure eight knot can be deformed to a different presentation which can then be rotated to its mirror image. So the figure eight knot is not a topological rubber glove. A symmetry presentation for the figure eight knot is illustrated in figure 4. We obtain the mirror image of this presentation by rotating this picture by 90° about an axis perpendicular to the page and which goes through the center of the picture. Here the mirror is again in the plane of the paper. Notice that the symmetry presentation of the figure eight knot has more crossings than that of the original picture of the figure eight knot in figure 3.

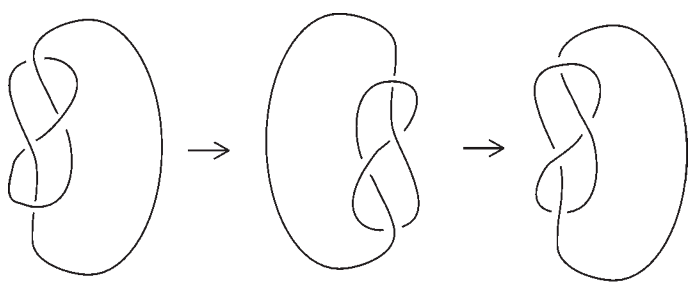


Figure 3. A deformation of a figure eight knot to its mirror image.

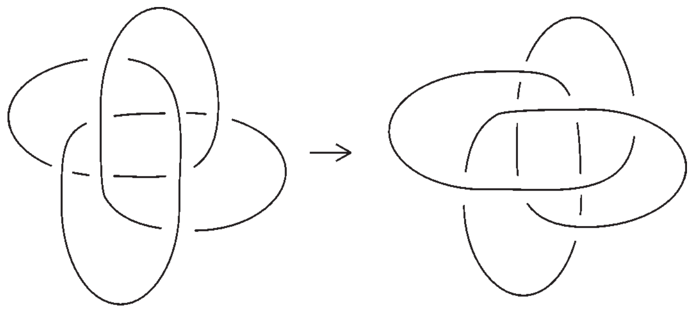


Figure 4. A symmetry presentation of the figure eight knot.

Since the figure eight knot is not an example of a topological rubber glove, we need to consider more complicated examples of knots or embedded graphs in order to find an example. By an embedded graph we mean a specific conformation of a graph in space up to deformation. That is, if one embedding of a graph can be deformed to another without any edges intersecting, then we consider these two embeddings to be the same. In particular, any molecular graph is considered to be an embedded graph. In this paper we shall present several types of examples of topological rubber gloves. First we present a knot which is a topological rubber glove, then we present a molecule which is a topological rubber glove, and finally, we present an embedded graph which is a topological rubber glove and has the additional property that no embedding of this graph can be rotated to its mirror image.

In order to be able to present our proofs we need to give mathematical definitions for all of our terminology.

Definition 1. Let $\mathbb{R}^3$ denote ordinary 3-space. Let A and B be subsets of $\mathbb{R}^3$. Let $h\colon A \to B$ be a continuous function which is a one-to-one correspondence, and has a continuous inverse. Then we say that h is a homeomorphism, and the sets A and B are homeomorphic. If there is a homeomorphism $h\colon \mathbb{R}^3 \to \mathbb{R}^3$ such that $h(A) = B$, then we write $h\colon (\mathbb{R}^3, A) \to (\mathbb{R}^3, B)$.

Intuitively, A and B are homeomorphic if creatures living in them who had no concept of distance could not tell one from the other. For example, a square and a circle of any size are homeomorphic, while a square and a line are not homeomorphic.

Definition 2. A simple closed curve is defined to be the homeomorphic image of the unit circle. A knot is defined to be any simple closed curve contained in $\mathbb{R}^3$. If a knot can be deformed into a plane it is called the unknot, otherwise it is called a non-trivial knot.

So a simple closed curve could be a wiggly or knotted circle. We see from this definition that when we refer to a knot we mean a knotted circle, we do not mean a knotted arc. For example, the figure eight knots which are illustrated in figures 3 and 4 are knots. Note that by definition there is a homeomorphism from a unit circle S^1 onto any knot K, however, such a homeomorphism from S^1 to K does not extend to a homeomorphism taking $\mathbb{R}^3$ to itself unless K is the unknot. Topologists often study knots in $S^3 = \mathbb{R}^3 \cup \{\infty\}$, as well as in $\mathbb{R}^3$. However, since we are interested in the connections between knot theory and chemistry, we restrict our attention to knots in $\mathbb{R}^3$.

Recall that Simon defined a molecular graph to be topologically achiral if it can be deformed to its mirror image and topologically chiral otherwise. In order to begin to formalize our notion of a topological rubber glove we need to introduce a more restricted type of achirality.

Definition 3. An embedded graph is said to be rigidly achiral if, when it is made flexible, it can be deformed to a position which can be rotated to its own mirror image. A topological rubber glove is an embedded graph which is topologically achiral but not rigidly achiral.

Some authors use the term rigid achirality to refer to the usual definition of chemical achirality for rigid molecules. However, we stick to the normal mathematical usage of the term. Accordingly, the concept of rigid achirality falls somewhere in between the usual definition of achirality for rigid molecules and the notion of topological achirality. In particular, an embedded graph which can be rigidly superimposed on its mirror image, is certainly rigidly achiral; and an embedded graph which is rigidly achiral can certainly be deformed to its mirror image, so it is topologically achiral. The figure eight knot is rigidly achiral since it can be deformed to the symmetry presentation which is illustrated in figure 4. On the other hand, the usual presentation of the figure eight knot, which is illustrated in figure 3, cannot be rigidly superimposed on its mirror image. So we need our figure eight knot to be flexible in order for it to attain its symmetry presentation.

To further understand the distinction between rigid achirality and chemical achirality, consider the molecules L-alanine and D-alanine which are illustrated in figure 5. Since these molecules are rigid, they are enantiomers. However, if the embedded graph of L-alanine is made flexible then it can be deformed to a planar presentation, which can be turned over to give us a planar presentation of D-alanine. Hence the embedded graphs illustrated in figure 5 are rigidly achiral according to our definition. From this example we see that this concept does not make sense for rigid molecules.

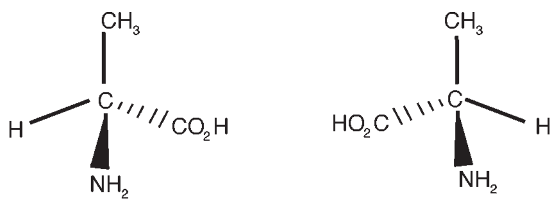


Figure 5. Enantiomers whose graphs are rigidly achiral according to our definition.

Rather the concept of rigid achirality, as we have defined it, is a topological concept which is intended for flexible or partially flexible graphs.

While the above definitions of topological achirality and rigid achirality capture the intuition behind the concepts, in order to prove some of our results we will need equivalent but more formal mathematical definitions. In particular, we would like to express the concept of topological achirality in terms of homeomorphisms. We begin by fixing a right handed orientation for $\mathbb{R}^3$. That is, if the first three fingers of a right hand are pointing in perpendicular directions, the thumb points in the direction of the positive x-axis, the pointer points in the direction of the positive y-axis, and the middle finger points in the direction of the positive z-axis. We say that a homeomorphism of $\mathbb{R}^3$ is orientation preserving if it takes right-handed orientations to right-handed orientations. If the homeomorphism takes right-handed orientations to left-handed orientations, then we say the homeomorphism is orientation reversing. For example, a reflection always takes a right-handed orientation to a left-handed orientation, so a reflection is orientation reversing. On the other hand, any translation or rotation is orientation preserving. Observe that the composition of two orientation reversing homeomorphisms is an orientation preserving homeomorphism, while the composition of an orientation reversing homeomorphism and an orientation preserving homeomorphism is an orientation reversing homeomorphism. With this terminology in mind we have the following mathematical definition of topological achirality.

Definition 4. Let G be a graph which is embedded in $\mathbb{R}^3$. Then G is topologically achiral if there is an orientation reversing homeomorphism $h: \mathbb{R}^3 \to \mathbb{R}^3$ such that $h(G) = G$. If no such homeomorphism exists, then we say that G is topologically chiral.

This definition is equivalent to the less formal definition which we gave earlier. In particular, if an embedded graph can be deformed to its mirror image then this deformation composed with a mirror reflection will give us an orientation reversing homeomorphism which takes the knot or graph back to itself. Before we define rigid achirality in terms of homeomorphisms we need one more preliminary definition.

Definition 5. Let $h: \mathbb{R}^3 \to \mathbb{R}^3$ be a homeomorphism. Let r be a natural number. We define h^r as the homeomorphism obtained by performing the map h repeatedly r times. If r is the smallest number such that h^r is the identity map, then we say that h has order r. If there is no such r then we say that h does not have finite order.

Any rigid motion which takes a graph to itself in 3-space has some finite order r. For instance, any reflection has order two, while a rotation of 120° about an axis has order three. A more complicated example of a finite order homeomorphism of $\mathbb{R}^3$ which may take a graph to itself is the following. First deform the graph to a symmetry presentation, then rotate and/or reflect it, then undo the deformation. For example, figure 6 illustrates a figure eight knot which we deform, then we rotate by

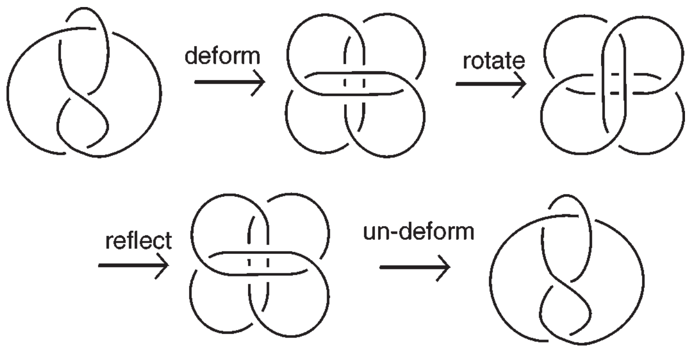


Figure 6. The figure eight knot has an orientation reversing homeomorphism of order four.

90° about a central axis which is perpendicular to the page, then we reflect through the plane of the paper, and finally, we undo the original deformation, taking the knot back to its original presentation. This illustrates an orientation reversing homeomorphism of order four which takes the figure eight knot to itself.

Our formal definition of rigid achirality is based on the idea of this last example.

Definition 6. Let G be a graph which is embedded in $\mathbb{R}^3$. Then G is said to be rigidly achiral if there is an orientation reversing finite order homeomorphism $h : \mathbb{R}^3 \to \mathbb{R}^3$ such that $h(G) = G$.

Any embedded graph which can be rotated to its mirror image or has a symmetry plane will be rigidly achiral according to this definition. Often, our orientation reversing finite order homeomorphism h will simply be a reflection or a rotation combined with a reflection. However, sometimes we will need to deform the graph to a symmetry presentation (as we did with the figure eight knot) before we reflect or rotate–reflect, and then undo the deformation. Our definitions of topological and rigid achirality using homeomorphisms are equivalent to our original definitions, however, they will be more convenient to use in certain proofs.

The first topological rubber glove which we will construct is a knot. It is often quite helpful to put an orientation on a knot. A knot orientation is simply an arrow placed on the knot specifying a particular direction along which the knot is traversed. Fixing an orientation on a knot allows us to distinguish between whether a homeomorphism $h : (\mathbb{R}^3, K) \to (\mathbb{R}^3, K)$ reverses or preserves the orientation of K. For example, if we orient a unit circle in the xy-plane, then a rotation of $\mathbb{R}^3$ about the z-axis will preserve the orientation of the circle, while a rotation about the x-axis will reverse the orientation of the circle. Note that whether h is an orientation reversing or preserving homeomorphism, and whether h reverses or preserves the orientation on K are totally independent. That is, we can have an orientation reversing homeomorphism which preserves or reverses the orientation on K, and we can have an orientation preserving homeomorphism which preserves or reverses the orientation on K. Specifying what h

does to the orientation of K allows us to distinguish two types of topologically achiral knots.

Definition 7. Let K be a knot in $\mathbb{R}^3$ and suppose that there is an orientation reversing homeomorphism $h:(\mathbb{R}^3,K)\to(\mathbb{R}^3,K)$. Given an orientation for K, if h preserves the orientation of K, then K is said to be positive achiral.

Definition 8. Let K be a knot in $\mathbb{R}^3$ and suppose that there is an orientation reversing homeomorphism $h:(\mathbb{R}^3,K)\to(\mathbb{R}^3,K)$. Given an orientation for K, if h reverses the orientation of K, then K is said to be negative achiral.

Figure 7 illustrates a knot which is both negative and positive achiral. The left-hand illustration shows that this knot has a vertical planar reflection which reverses the orientation of the knot. This planar reflection is an orientation reversing homeomorphism, so the knot is negative achiral. The right-hand illustration shows that we can rotate the knot by 180° about a central axis, perpendicular to the plane of the paper, and then reflect through the plane of the paper to obtain the original knot. This rotation–reflection combination is an orientation reversing homeomorphism which preserves the orientation on K. So K is positive achiral.

Any orientation reversing homeomorphism which takes a knot to itself will either preserve or reverse the orientation on the knot. So any topologically achiral knot must either be positive achiral or negative achiral. Of course a knot can be both positive and negative achiral, by using two different homeomorphisms, as in figure 7.

We say that a knot is rigidly negative achiral or rigidly positive achiral in $\mathbb{R}^3$ if the homeomorphisms in the above two definitions have finite order. We saw from figure 6 that the figure eight knot has an orientation reversing homeomorphism of order four. If we put an orientation on the knot, then this homeomorphism will preserve the orientation of the knot. So the figure eight knot is rigidly positive achiral. The

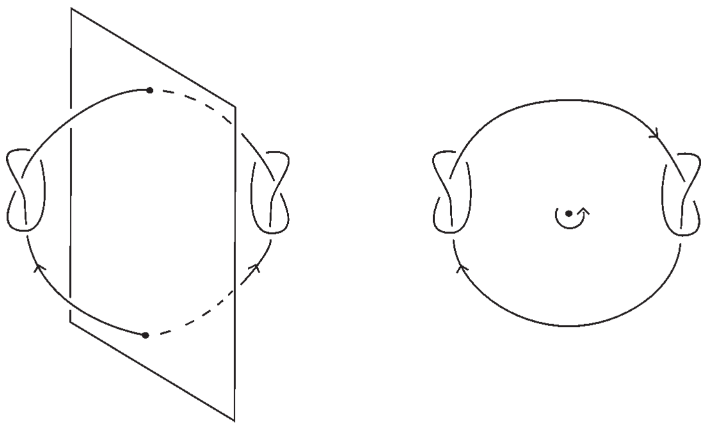


Figure 7. A knot which is both positive and negative achiral.

knot illustrated in figure 7 is actually both rigidly positive achiral and rigidly negative achiral, since the reflection on the left and the rotation–reflection on the right both have order two. Any rigidly achiral knot must be either rigidly negative achiral or rigidly positive achiral. We shall prove shortly that any rigidly negative achiral knot looks roughly like the knot in figure 7. To better describe the type of knot illustrated in figure 7, we need yet another definition.

Definition 9. Let K be a knot, and suppose that there exists a subset F of $\mathbb{R}^3$ which is homeomorphic to a plane and which meets K in two points p and q. Let B be an arc in F with endpoints p and q. Consider the simple closed curves obtained by joining each of the components of $K - \{p, q\}$ to the arc B. If neither of these simple closed curves is the unknot then we say that K is a connected sum.

The left hand picture in figure 7 illustrates the plane in this definition. We can take B to be any arc in the plane joining the two points where K meets the plane. In this case, the two knots we get in this way are both trefoil knots, though one is the mirror image of the other. Hence the knot in figure 7 is a connected sum.

We would like to prove that any rigidly negative achiral knot in $\mathbb{R}^3$ is a connected sum. In order to prove this, as well as most of the other results in this paper, we will use the classification of fixed point sets of finite order homeomorphisms, which was developed by P.A. Smith in 1939 [15].

The fixed point set of a homeomorphism $h : \mathbb{R}^3 \to \mathbb{R}^3$ is the set of all points x such that $h(x) = x$. For example, any reflection of $\mathbb{R}^3$ will have fixed point set a plane and any rotation of $\mathbb{R}^3$ will have fixed point set the line which is the axis of the rotation. A combination of a reflection and a rotation about an axis perpendicular to the plane of reflection will fix only the point where the axis of rotation meets the plane of reflection. Let $h : \mathbb{R}^3 \to \mathbb{R}^3$ be a finite order homeomorphism. If h is orientation preserving, then Smith theory states that the fixed point set of h must be homeomorphic to a line. Roughly speaking, this means that h can be obtained by deforming, then rotating, then undoing the deformation. If h is orientation reversing, then Smith theory states that the fixed point set of h is either one point or is homeomorphic to a plane. Roughly speaking, this means that h can be obtained by deforming, then rotating and reflecting or just reflecting, then undoing the deformation. Even prior to Smith theory, the fixed point sets of finite order homeomorphisms of simple closed curves were well understood. Suppose that h has finite order and K is a simple closed curve such that $h(K) = K$. If h preserves the orientation of K then h cannot fix any point of K. On the other hand, if h reverses the orientation of K then h will fix precisely two points of K. We shall use Smith theory to prove the following theorem.

Theorem 1 ([3]). If a non-trivial knot is rigidly negative achiral in $\mathbb{R}^3$, then it is a connected sum.

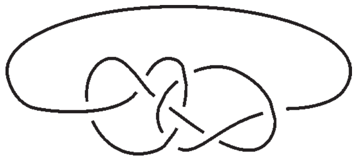


Figure 8. The knot 8_{17} is a topological rubber glove.

Proof. Suppose that K is a non-trivial knot which is rigidly negative achiral in $\mathbb{R}^3$. Pick an orientation for K and let $h:(\mathbb{R}^3, K) \to (\mathbb{R}^3, K)$ be a finite order orientation reversing homeomorphism which reverses the orientation on K. Since h reverses the orientation on K and h has finite order, h must fix two points of K. So, let p and q be the fixed points of h on K. Since h is a finite order orientation reversing homeomorphism of $\mathbb{R}^3$, by Smith theory the fixed point set of h is either one point or is a set homeomorphic to a plane. We already know that the points p and q are contained in the fixed point set of h, so the fixed point set of h must be a set F which is homeomorphic to a plane. Since h is orientation reversing and h fixes each point of F, it must exchange the two components of $\mathbb{R}^3 - F$. Let B be any arc in F with endpoints p and q, and let K_1 and K_2 be the simple closed curves obtained by joining each of the components of $K - \{p, q\}$ to the arc B. The homeomorphism h interchanges the two components of $K - \{p, q\}$ and fixes every point of B. So, h exchanges K_1 and K_2. Thus either both K_1 and K_2 are knotted (and one knot is the mirror image of the other) or neither is knotted. If neither were knotted, then K would be the unknot, contrary to hypothesis. Hence both K_1 and K_2 must be knotted. Therefore by definition, K is a connected sum. □

Theorem 1 allows us to construct an example of a knot which is a topological rubber glove in $\mathbb{R}^3$. To do this, we pick a knot which is not a connected sum and which is negative achiral but not positive achiral. The simplest such knot is the knot 8_{17} which is illustrated in figure 8. Unlike the trefoil knot and the figure eight knot, most knots do not have names. Rather, knots are referred to by numbers. This knot is called 8_{17} because eight is the minimum number of crossings any projection of it can have, and this knot is the seventeenth knot with eight crossings which is listed in the standard knot tables. See, for example, the tables in Rolfsen's book [13].

Kawauchi proved that 8_{17} is not positive achiral [8]. We can see that this knot is negative achiral by the deformation of it to its mirror image illustrated in figure 9. We first rotate the knot by 180° about an axis which is perpendicular to the plane of the paper, then we pull the long arc from the bottom of the knot to the top of the knot. This final knot is the reflection of the first knot through the plane of the paper. If we followed this deformation by a mirror reflection through the plane of the paper, then we would get our original diagram of 8_{17}, with the orientation on the knot reversed. Thus the knot is negative achiral, which means in particular that it is topologically achiral.

Since 8_{17} is not a connected sum it cannot be rigidly negative achiral by theorem 1. It is not positive achiral, so it is certainly not rigidly positive achiral. Hence 8_{17}

Figure 9. A deformation of the knot 8_{17} to its mirror image.

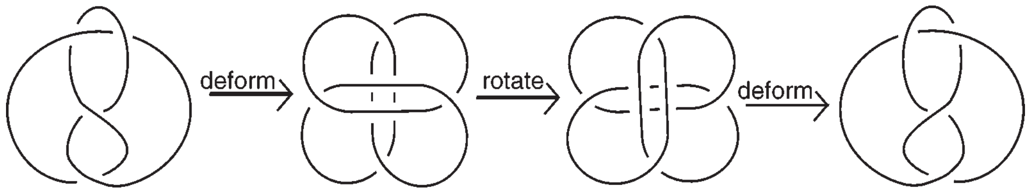


Figure 10. We deform the figure eight backbone to a symmetry presentation, then rotate, and then deform back to get the mirror image.

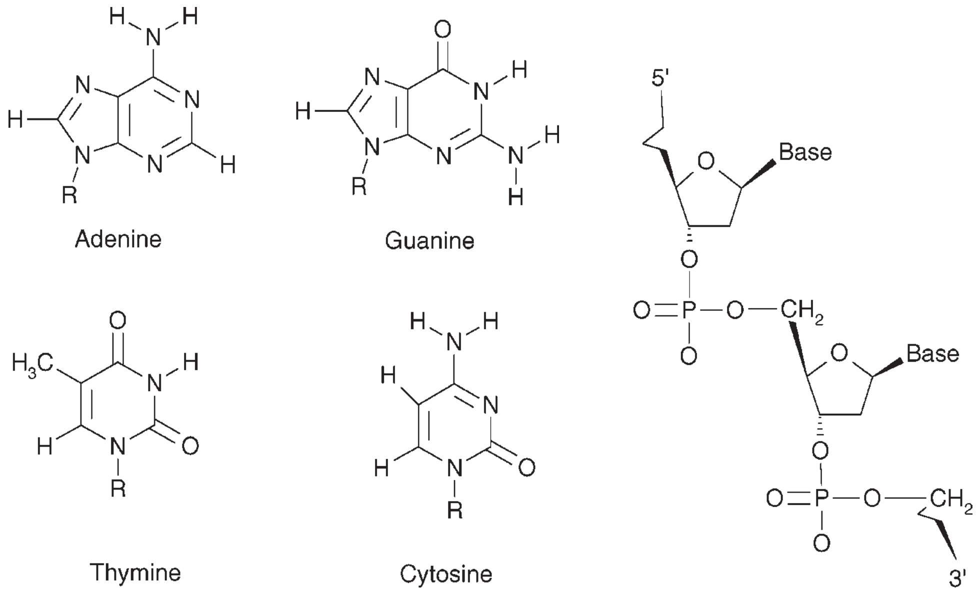
is topologically achiral but not rigidly achiral. Therefore 8_{17} is a topological rubber glove.

While the knot 8_{17} shows us that topological rubber gloves can exist as topological objects, this knot is not a molecular bond graph. For many years after it was known that knots and graphs could be topological rubber gloves, there was still no known molecular structure which was a topological rubber glove. In 1992, Du and Seeman [2] synthesized a single stranded DNA figure eight knot, whose graph was shown in 1995 to be a topological rubber glove [6]. The global structure of this synthetic single stranded DNA molecule is a figure eight knot, but locally the molecular graph is made up of 66–104 nucleotide subunits each containing a phosphate, a sugar, and one of the four bases cytosine, thymine, adenine, and guanine.

Theorem 2 ([6]). The graph of the single stranded synthetic DNA figure eight knot is a topological rubber glove.

Proof. We use our original definition to see that this molecular graph is topologically achiral. First, deform the graph so that the sugars and bases all lie in the plane of the paper which contains the phosphates. Figure 10 illustrates a deformation of the figure eight backbone to a symmetry presentation, which can be rotated by 90°, to obtain its mirror image. After this rotation, we can then deform the backbone back to the mirror image of its original embedding. Rotating the backbone of the molecular graph has the side effect of moving the bases to new positions relative to the knot. However, we can now slither the structure along itself until each base is back to its original position. Finally, tilt the sugars and bases as necessary so that their angles will be the mirror image of what they were to start. Thus the molecular bond graph of the DNA figure eight knot is topologically achiral.

Let K denote the molecular graph of the DNA figure eight knot. We will prove that K is not rigidly achiral using the definition in terms of homeomorphisms. Suppose



(a) (b)

Figure 11. (a) DNA bases. (b) DNA backbone.

that there exists an orientation reversing finite order homeomorphism $h:(\mathbb{R}^3, K) \to (\mathbb{R}^3, K)$. As can be seen from figure 11(a), the bases cytosine, thymine, adenine, and guanine all have distinct molecular graphs. (The letter R in the figure indicates where each base is attached to the backbone.) It follows that h must take each base to a base of the same type.

For simplicity, we can think of K as a figure eight knot with vertices labelled C, T, A and G, where h takes K to itself sending each vertex to a vertex which is labelled with the same letter. Since the figure eight knot is homeomorphic to a circle and h has finite order, h either reflects or rotates the vertices around the figure eight knot. But the bases in the DNA figure eight knot do not occur in a sequence which is the same when read forwards or backwards. So, h cannot reflect the bases within the backbone. Also, the bases do not occur in a sequence which systematically repeats itself around the backbone. So, h cannot non-trivially rotate the bases around the backbone. Therefore, h is a trivial rotation (that is, a rotation by zero degrees), and so h must send each base to itself. We can see from the bases drawn in figure 11(a) and the backbone drawn in figure 11(b), that this means that h must fix every point of the entire molecular graph except possibly for some hydrogen atoms.

Recall that h is a finite order orientation reversing homeomorphism of $\mathbb{R}^3$. So, by Smith theory, the fixed point set of h is either one point or is homeomorphic to a plane. If h fixes every point of the graph except some hydrogen atoms, then the fixed point set of h cannot be a single point. Thus the molecular graph must be contained in a set which is homeomorphic to a plane. This is impossible since the graph has the global structure of a figure eight knot, and only an unknot can lie in a plane. So no such homeomorphism can exist. Therefore, the synthetic single stranded DNA figure eight knot is a topological rubber glove. □

Note, that while the DNA figure eight knot is topologically achiral, it is not chemically achiral since the sugars and bases cannot tilt themselves into the required angles.

In both of the examples we have given so far of topological rubber gloves, it is the particular embedding of the graph which prevents the graph from being rigidly achiral. That is, there are different embeddings of the graphs (i.e., different conformations) which are rigidly achiral. In particular, as an abstract graph, independent of its embedding in space, the knot 8_{17} is homeomorphic to a circle. So the graph of 8_{17} can be reembedded so that it is now an ordinary circle lying in a plane. In other words, the knot 8_{17} and a planar circle are topological stereoisomers. We can similarly reembed the graph of the single stranded DNA figure eight knot so that its backbone is unknotted and the graph lies in a plane. Any graph which is embedded in a plane is rigidly achiral, since reflection through the plane containing the graph is a finite order orientation reversing homeomorphism taking the graph to itself. So both of our topological rubber gloves can be reembedded so that they become rigidly achiral. It is natural to ask whether there can exist a topological rubber glove, which has the additional property that there does not exist any embedding of the graph which is rigidly achiral. Such a graph would necessarily have the property that no embedding of it could lie in a plane.

An abstract graph which cannot be embedded in a plane is said to be a non-planar graph. Kuratowski proved that a graph is non-planar if and only if it contains either the bipartite graph on three vertices $K_{3,3}$ or a complete graph on five vertices K_5, each with the possible addition of some extra vertices [9]. We illustrate $K_{3,3}$ and K_5 in figure 12. We have drawn these graphs abstractly, without specifying how they are embedded in space. In particular, these pictures are not meant to indicate that the edges intersect. The edges of an embedded graph are never permitted to intersect.

Using a specific embedding of a four rung Möbius ladder we shall construct a topological rubber glove which has the property that no embedding of it is rigidly

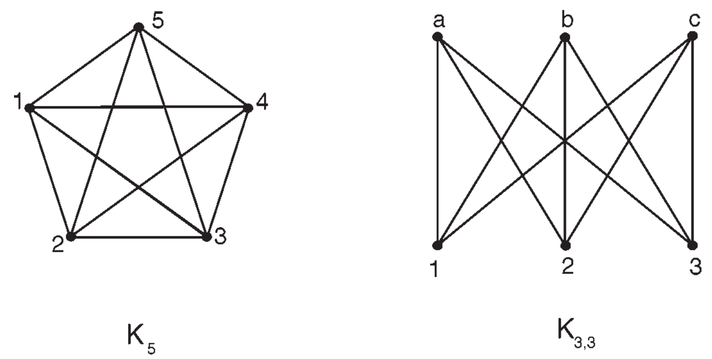


Figure 12. Any non-planar graph contains a graph homeomorphic to one of these two graphs.

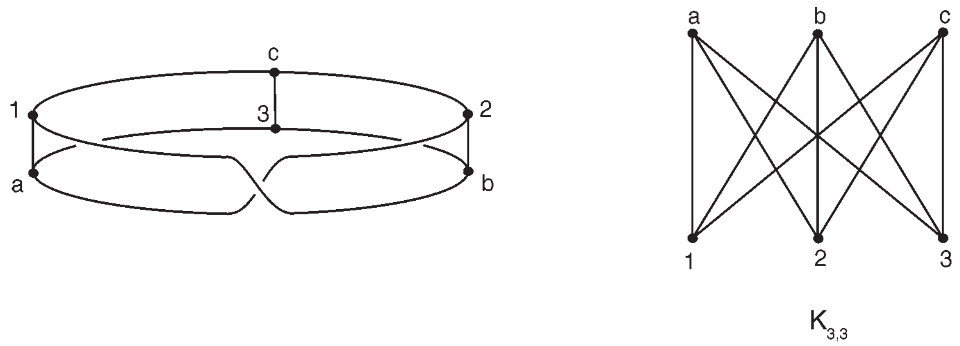


Figure 13. A molecular Möbius ladder with three rungs is an embedding of $K_{3,3}$.

achiral. We can see that the three rung Möbius ladder is non-planar because it is actually a $K_{3,3}$ graph. The vertices of the Möbius ladder in figure 13 have been labelled $1, 2, 3$ and a, b, c in order to help the reader see this $K_{3,3}$. The four rung Möbius ladder is also a non-planar graph, since it contains the three rung Möbius ladder.

Recall that Simon proved that the embedded graph of any molecular Möbius ladder with at least three rungs is topologically chiral. Simon's results led to the question of whether the chirality of the molecular Möbius ladder is due to the intrinsic structure of the graph or to the specific embedding of the graph in the form of a Möbius strip. In answer to this question we proved that every embedding of a Möbius ladder with an odd number of rungs greater than one is topologically chiral, but every Möbius ladder with an even number of rungs has a rigidly achiral embedding [4]. We shall use a rigidly achiral embedding of a four rung Möbius ladder for our construction.

In order to understand the different ways that a Möbius ladder can be embedded in $\mathbb{R}^3$, we first have to understand the abstract graph of a Möbius ladder with n rungs, which we shall denote by M_n. The first picture in figure 14 is the standard embedding of a molecular Möbius ladder with three rungs. We can see from this picture that there is an edge connecting vertex 1 to 2, 2 to 3, and so on, up to vertex 6, which is connected back to vertex 1. Thus any embedding of M_3 includes a simple closed curve consecutively containing these six vertices. In addition, M_3 has edges connecting vertices 1 to 4, 2 to 5 and 3 to 6. This means that opposite vertices on the circle are connected by edges. The second picture in figure 14 illustrates a different embedding of M_3. In general, any embedding of M_n contains a simple closed curve K with $2n$ vertices, and rungs $\alpha_1, \alpha_2, \ldots, \alpha_n$ connecting opposite vertices on K.

In figure 15 we illustrate an embedding of M_4 which is rigidly achiral. The horizontal circle is the simple closed curve K containing eight vertices which are the endpoints of the four rungs labelled α_1, α_2, α_3 and α_4. We rotate this embedding of M_4 by 90° about a vertical axis in order to obtain its mirror image through a horizontal plane containing K. This 90° rotation together with a mirror reflection through the plane takes K to itself, exchanging the rung α_1 with the rung α_3, and exchanging the rung α_2 with the rung α_4. This rotation–reflection is an order four orientation reversing

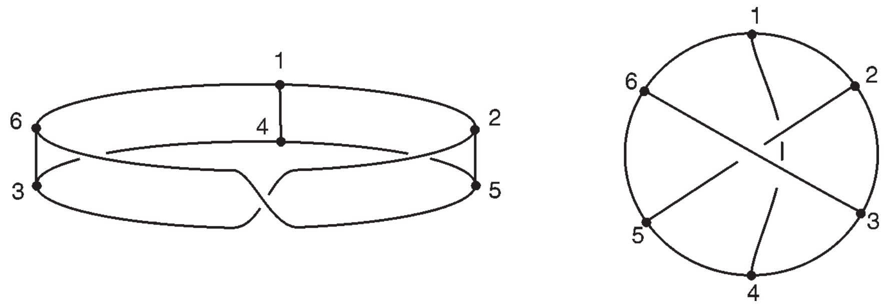


Figure 14. Two embeddings of M_3.

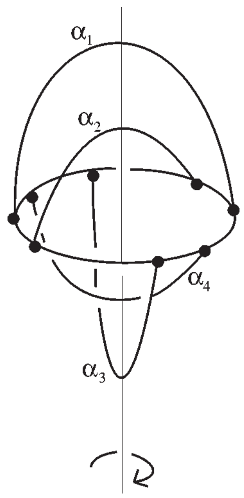


Figure 15. An achiral embedding of a Möbius ladder with four rungs.

homeomorphism of $\mathbb{R}^3$ which takes M_4 to itself. So this embedding of M_4 is rigidly achiral. By adding symmetric pairs of rungs above and below the plane, we can create a similar achiral embedding for any Möbius ladder with an even number of rungs.

We shall consider the embedded graph G illustrated in figure 16. The embedded graph G is made up of the rigidly achiral Möbius ladder with four rungs M of figure 15, joined to a planar triangle T by two edges e_1 and e_2. We see as follows that this graph is topologically achiral. First, notice that we can rotate the Möbius ladder M like a bead on a necklace, without moving the rest of the graph. If we rotate M by 90° while fixing T, e_1 and e_2, we will obtain the mirror image of G through a horizontal mirror, as we did in figure 15. Let h denote this 90° rotation of M which fixes T, e_1 and e_2, composed with a reflection through a horizontal plane containing the central circle of M and the vertex v. Then h will be an orientation reversing homeomorphism of $\mathbb{R}^3$ which takes G to itself. Observe that h reflects the whole graph, but only rotates the left-hand side. So, h does not have finite order. We will prove below that neither this embedding of G nor any other is rigidly achiral.

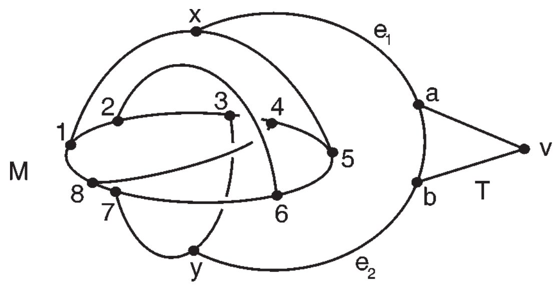


Figure 16. This embedding of G is topologically achiral but no embedding of G is rigidly achiral.

Theorem 3 ([5]). The embedding of G in figure 16 is a topological rubber glove, and no embedding of G is rigidly achiral.

Proof. We saw above that the embedding of G in figure 16 is topologically achiral. Now we will prove that no embedding of G is rigidly achiral. Suppose that G is embedded in $\mathbb{R}^3$ in such a way that there exists a finite order orientation reversing homeomorphism $h:(\mathbb{R}^3, G) \to (\mathbb{R}^3, G)$. Based on this assumption we shall obtain a contradiction by arguing purely on the basis of intrinsic properties of the graph, without making any assumptions about any particular embedding of G.

The homeomorphism h preserves the structure of the graph. This means that h takes adjacent vertices to adjacent vertices. By analyzing the structure of the different parts of the graph, we see that we must have $h(M) = M$, $h(T) = T$, $h(e_1 \cup e_2) = e_1 \cup e_2$ and $h(v) = v$, though h does not necessarily fix each point of these sets. Furthermore, h must either fix or interchange the two vertices a and b, and in either case, h fixes a point in the middle of the edge from a to b. Also the vertices x and y have the unique property that removing them would disconnect the subgraph M from e_1 and e_2. So, h must also take x and y to themselves or to each other. It follows that h sends every odd numbered vertex to an odd numbered vertex and every even numbered vertex to an even numbered vertex. This implies that h takes every edge which has one odd and one even vertex to an edge which has one odd and one even vertex. Let K denote the simple closed curve which consecutively goes through the vertices 1–8. We see from the above that h takes K setwise to itself.

Observe that the fixed point set of h contains at least the point v and one point on the edge between a and b. Since h is a finite order orientation reversing homeomorphism of $\mathbb{R}^3$, it follows from Smith theory that the fixed point set F of h is homeomorphic to a plane. Since h takes the circle K to itself, either K is contained in F or K intersects F in two points. First, suppose that K is contained in F. Then every point on K is fixed by h. Each of the vertices of K has precisely one edge which is not contained in K. Since h takes edges to edges and h fixes each vertex on K, it follows that h must take each of the edges joined to K to themselves. By hypothesis, h has finite order, so this means that h pointwise fixes every edge with a vertex on K. It follows that all of the subgraph M is contained in F, the fixed point set of h. But this is impossible since M is a Möbius ladder with four vertices, and hence is non-planar. Therefore, K cannot be contained in the plane F.

Thus, K must meet F in two points, say a and b, which may or may not be vertices of K. Let i and j be the vertices on K which are on either side of the point a. Observe that the numbers i and j differ by one if a is not a vertex and by two if a is a vertex. In either case, $j \neq i + 4$. Now h interchanges vertices i and j. Since $i + 4$ is four vertices from i going around either direction and $j + 4$ is four vertices from j going around either direction, h must also interchange vertices $i + 4$ and $j + 4$. Let p be the arc going from i to $i + 4$ consisting of one or two edges, and let q be the arc going from j to $j + 4$ consisting of one or two edges. So, p and q may or may not contain x and y. Then p and q are disjoint arcs, and h interchanges p and q. Figure 17 illustrates K together with the vertices i, j, $i+4$, and $j+4$, and the edges containing them, where additional vertices and edges have been omitted from the drawing. The arcs p and q in figure 17 are not meant to intersect, rather the illustration represents a portion of our abstract graph G independent of any particular embedding.

We know that h interchanges the two components of $\mathbb{R}^3 - F$, hence h interchanges the two components of $K - \{a, b\}$. So each component of $\mathbb{R}^3 - F$ contains an arc of $K - \{a, b\}$, and h interchanges the vertices in one of these arcs with the vertices in the other arc. Since there are eight vertices on K and they are numbered consecutively, it follows that the vertices i and $i+4$ cannot both be in the same component of $\mathbb{R}^3 - F$. So the arc p from i to $i + 4$ must intersect the fixed point set F. Now the point of intersection of p and F must be fixed by h. Since the arcs p and q are disjoint this means that h cannot interchange p with q. Hence K cannot meet F in two points.

Therefore, no matter how G is embedded in $\mathbb{R}^3$ there is no finite order orientation reversing homeomorphism of $\mathbb{R}^3$ taking G to itself. Hence G has no embedding which is rigidly achiral. □

It follows from this theorem that no topological stereoisomer of G can be rotated to its mirror image or has a plane of symmetry.

If every embedding of a graph has a certain property then that property is said to be intrinsic. The example of theorem 3 has the intrinsic property that no embedding of it is rigidly achiral. Observe as follows that there cannot exist a graph such that

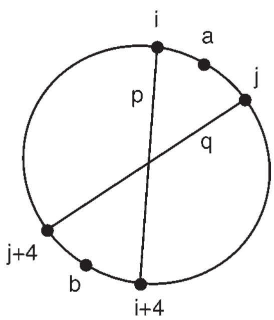


Figure 17. K together with the arc p going from i to $i + 4$ and the arc q going from j to $j + 4$.

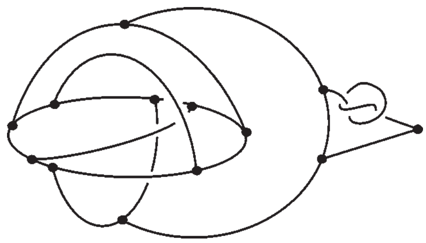


Figure 18. A topologically chiral embedding of G.

every embedding is a topological rubber glove. Any graph which does not contain a simple closed curve has a planar embedding which is rigidly achiral, and hence is not a topological rubber glove. On the other hand, any graph which contains a simple closed curve has knotted embeddings which are topologically chiral and hence these embeddings are not topological rubber gloves. For example, we could tie a little knot in one edge of the graph G to create a topologically chiral embedding (see figure 18). So our topological rubber glove of theorem 3 is as intrinsic a topological rubber glove as we could hope to find.

As a final note, Chambron et al. [1] have recently designed and synthesized an entirely new kind of topological rubber glove. Their molecule is a catenane which has the property that it is chemically achiral but not rigidly achiral. Chemical achirality implies topological achirality, so their molecule is indeed a topological rubber glove. This molecule is noteworthy both because it is the first molecule which is a topological rubber glove that is not made from DNA, and because it is the first topological rubber glove which is actually chemically achiral.

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