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All toroidal embeddings of polyhedral graphs in 3-space are chiral†

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Received (in Montpellier, France) 16th April 2009, Accepted 26th June 2009
First published as an Advance Article on the web 4th August 2009
DOI: 10.1039/b907338h

We investigate the possibility of forming achiral knottings of polyhedral (3-connected) graphs whose minimal embeddings lie in the genus-one torus. Various analyses to show that all examples are chiral. This result suggests a simple route to forming chiral molecules *via* templating on a toroidal substrate.

Published on 04 August 2009 on http://pubs.rsc.org | doi:10.1039/B907338H
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I. Introduction

The interplay between structural chemistry, graph theory and knot theory is a rich area for chemists and mathematicians alike. The founder of topology, Johann Listing, noted the possibility of chiral knots in 1847;[1] a year later Pasteur published his landmark paper on the optical activity of ammonium tartrate crystals. Indeed, knot theory began following early studies on molecular isomerism. More recently, the investigation of chirality and knotting in organic molecules and DNA complexes using graph theoretical techniques has led to a number of fruitful results. In particular, chemists now speak of *topological chirality*, characterised by non-superimposable 3D mirror images of graphs among all possible embeddings of the graph that preserve ambient isotopy.[2]

Entangled (and, more specifically knotted) graphs or nets have generated considerable interest in synthetic organic chemistry.[2–12] More recently, the possibility of entanglement and knotting has been raised in extended framework coordination polymer materials.[13] This paper describes a strong interplay between tangled nets and the notion of chirality. We look at simple graphs whose topologies are those of the edges of polyhedra, such as the network of edges in an octahedron or icosahedron. (We define these 'polyhedral graphs' more precisely below.)

The simplest realisations of polyhedral graph topologies in space form a network of edges that can be smoothly deformed to reticulate a sphere. Many of these cases are achiral; for example among the edge-graphs of the 5 Platonic and 13 Archimedean polyhedra, only the snub cube and the snub dodecahedron are (topologically) chiral.[14] We can however, *tangle* the network, so that it remains topologically polyhedral, but no longer reticulates a sphere. The simplest entanglements reticulate the donut-shaped torus rather than the sphere. To our surprise, we have failed to generate a single example of a toroidal polyhedral graph that is achiral. We conjecture here that *all* toroidal entanglements of polyhedral graphs are chiral. The conjecture is proven provided the entanglement contains a knot or a link.

For convenience here, we refer to the family of embeddings of a graph that preserve ambient isotopy – *viz*. all possible realisations of the graph can be deformed into each other without passing edges through each other – as *isotopes*. For a given graph, there exist an unlimited number of distinct isotopes, partially characterised by the presence of distinct families of knots and links within minors of the graph. (The minor of a graph results when vertices are removed, along with the edges that connect to them, or if edges are deleted, or contracted so that their endpoints merge.) We have recently suggested a ranked enumeration schema for isotopes based on embeddings of the isotope within orientable 2-manifolds of increasing topological complexity.[15] We describe the *genus* of the isotope as being equal to that of the (topologically) simplest orientable manifold that can be reticulated by the isotope such that no disjoint edges in the isotope cross in the manifold, also referred to as the 'minimal embedding' of the isotope. That approach is particularly suited to the enumeration of *polyhedral graphs*, *i.e*. 3-connected planar simple graphs.[16] A 3-connected graph is one that can have no fewer than three vertices (and attendant edges) removed before it forms two or more disconnected components. (We note in passing that if the connectivity of the graph is larger than three, it is also 3-connected.) A simple graph is one in which there is a maximum of one edge between any pair of vertices; while a planar graph is one that can be embedded in the plane (or equivalently the sphere) without edge crossings. The simplest – unknotted – embedding of finite polyhedral graphs is in the 2D sphere, $\mathbb{S}^2$. Higher-order isotopes embed in the genus-one torus (the donut), the genus-two torus (the 'bitorus'), *etc*. A preliminary account of this approach has been published recently[17] and a fuller account, dealing with genus-one toroidal embeddings of the tetrahedral, octahedral and cube graphs, is in preparation.[15]

Here we focus on embedded graphs that result from reticulations of the torus by polyhedral graphs, embedded in 3-space in the standard manner (as a donut). We consider only those isotopes that cannot be realised by spherical reticulations; we call these 'toroidal isotopes' and describe the toroidal reticulation as a 'minimal embedding'.

The tetrahedral graph is the simplest polyhedral graph. Evidently, the standard embedding of the unknotted

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† Electronic supplementary information (ESI) available: Discussion of toroidal reticulation: Fig. 1: Film 1. Selected frames of the computer animation showing the formation of a toroidal isotope (bottom right) from its universal cover (top left). See DOI: 10.1039/b907338h

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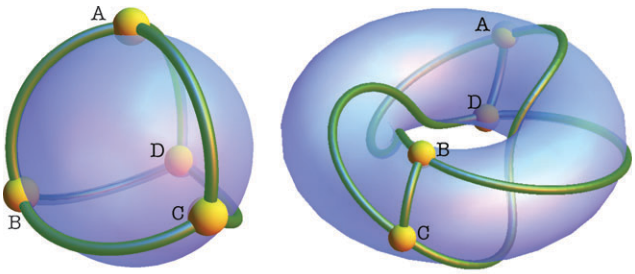


(a) (b)

Fig. 1 (a) The unknotted tetrahedral graph, which embeds in the 2D sphere, $\mathbb{S}^2$. (b) The simplest knotted tetrahedron contains a single trefoil (ABCDCA).

tetrahedral graph is derived from the edges of the 'spherical tetrahedron' in $\mathbb{S}^2$, Fig. 1. An infinite number of toroidal tetrahedral graphs are possible. The simplest example contains a single trefoil knot as a subgraph, as shown in Fig. 1. The trefoil winds around the two fundamental cycles of the torus three times in one direction and twice in the other. We therefore associate the trefoil with a torus winding of homotopy $\{3, 2\}$ or $\{2, 3\}$ (and negatives thereof). (A visualisation of the relationship between torus knots and their homotopy type is available on the web.[18]) In common with all torus knots, the trefoil is chiral.[19] To determine whether this tetrahedron embedding is chiral, we use Kauffman's topological invariant that consists of all cycles in the knotted graph; if this contains only chirally knotted or linked cycles (of the same hand), chirality of the isotope is assured.[20] The tetrahedral graph contains seven distinct cycles, labelled according to Fig. 1 *ABCA*, *ACDA*, *ABDA*, *BCDB*, *ABCDA*, *ACBDA* and *ABDCA*. Among those cycles, six are trivial knots and one (*ABDCA*) is a trefoil, showing that this tetrahedral isotope is indeed chiral.

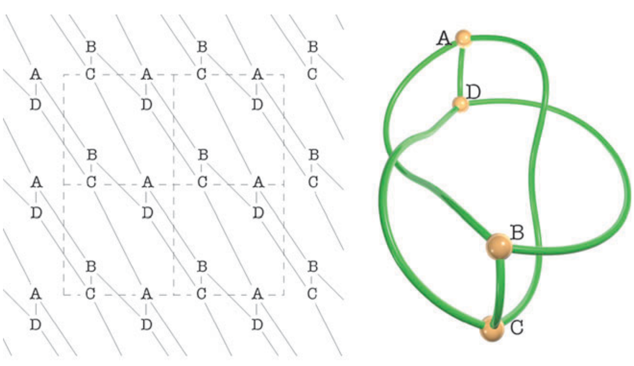
II. The universal cover of toroidal isotopes

Toroidal isotopes can be 'unrolled' into the universal cover of the torus, the Euclidean plane, $\mathbb{E}^2$. The universal cover offers a simple route to construction of toroidal isotopes containing specified knots – a tool that we shall use below to search for achiral toroidal isotopes. Rings or cycles in the graph can be deduced from the universal cover, as follows: 'Null homotopic' cycles on the torus map to cycles in the cover. Alternatively, cycles that form collars around the torus with non-trivial (non-null) homotopies are found by traversing edges in the cover across unit cells. Any path from a vertex to its image in an adjacent cell (*e.g.* between matching vertices of any colour in Fig. 3, 7 and 8) is a non-null homotopic cycle whose homotopy type is given by the vector (p, q) linking the sites. A single copy of the torus rolls into a single unit cell of the 2-periodic pattern of edges of the isotope in $\mathbb{E}^2$; additional unit cells are generated by further unrolling of the torus. Smallest lattice vectors a, b of the periodic pattern correspond to the shortest loops around the pair of distinct cycles (of meridian and longditude) in the torus, related to the generators of the torus' fundamental group. The procedure is illustrated by a simple animation contained in the ESI.† An example of the universal cover of the simplest toroidal tetrahedral isotope is illustrated in Fig. 2.

In the universal cover, cycles in the graph that wind around those two fundamental cycles $\{p, q\}$ times respectively can be represented by a vector (p, q) with respect to the axes generated by the basis of the a and b vectors. When p and q are coprime and of size at least 2, the resulting loop is a torus knot and thus is necessarily chiral. If p and q have a common factor k, then a link with k components results. These torus links are also chiral, for all cases except the Hopf link, which contains a pair of loops of homotopy type $\{\pm 1, \pm 1\}$.

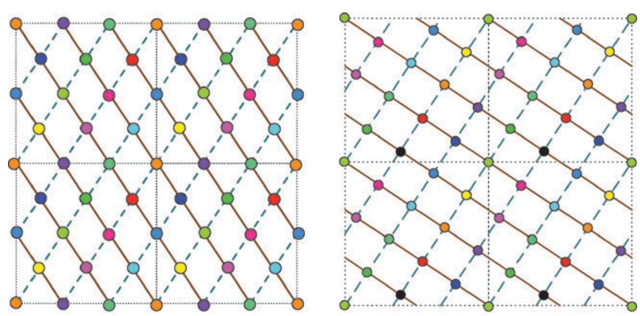
Enumeration of numerous tangled toroidal embeddings of tetrahedra, octahedra and cube graphs by us have failed to produce a single example of an achiral toroidal isotope.[15,17] Those failures motivated us to attempt to prove that all toroidal isotopes of polyhedral graphs are chiral, as follows.

We use Kauffman's topological invariant,[20] which for achiral isotopes requires that every chiral cycle within the isotope must be paired with an equivalent cycles of opposite hand. Our proof that minimally toroidal polyhedral isotopes are chiral relies on a conjecture that there are no genus-one entanglement modes of a polyhedral graph that reticulate a torus other than those containing knots or links. We note here that other entanglement modes free of knots or links can exist



(a) (b)

Fig. 2 (a) A part of the universal cover of the simplest knotted tetrahedral graph. The graph embeds in the torus by gluing up a single unit cell of the universal cover, joining edges defined by lattice vectors, to form the pattern shown in Fig. 1(b). (b) The resulting embedding in three-dimensional space, $\mathbb{E}^3$.



(a) Isotope *A* (b) Isotope *B*

Fig. 3 A part of the universal covers of simplest graphs containing a pair of chiral trefoils forming achiral toroidal isotopes: (a) $\{2, 3\} \otimes \{2, -3\}$ and (b) $\{2, 3\} \otimes \{3, -2\}$ homotopy-type trefoils, *i.e.* left- and right-handed trefoil knots. The enantiomers are distinguished by the full (brown) and dashed (blue) lines.

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within isotopes of genus two and higher, such as the examples in ref. 21, however none of these more exotic species of entanglement have been found for genus one.

Since we consider only polyhedral isotopes which are minimally embedded on the torus, by the above conjecture, we require that the isotope contain a (torus) knot or link. It is known that such knots and links are chiral, except for the Hopf link. Achiral isotopes which contain chiral knots or links necessarily contain their chiral enantiomeric partners. We show by construction that such isotopes cannot be polyhedral, as their graph cannot be embedded in the plane. A separate argument in Section V also prohibits isotopes containing Hopf links. These arguments logically consist of two parts: firstly the graph minors containing just the relevant knots or links are shown to be non-planar, then the general case of *any* graph containing these minors is shown to be non-planar through an application of Kuratowski's theorem (Section III).

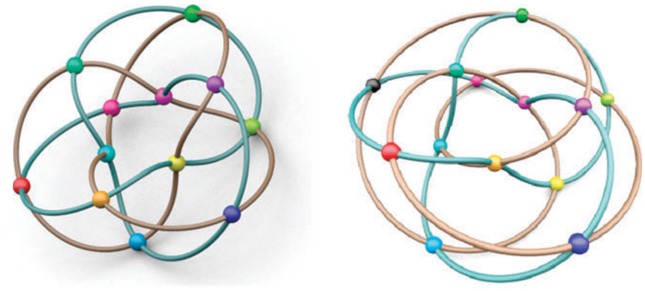
III. Toroidal isotopes composed of gemini pairs of trefoil knots

An obvious route to construction of a potentially achiral toroidal isotope is to combine pairs of opposite-handed trefoil knots, giving a graph whose vertices correspond to the intersections of the loops. As each trefoil is chiral, such a combination will involve a trefoil with homotopy $\{2,3\}$, coupled with the opposite handed knot with homotopy $\{2,-3\}$ or $\{3,-2\}$. We call this pairing a *gemini pair* of knots and denote it $\{2,3\}\otimes\{2,-3\}$ and $\{2,3\}\otimes\{3,-2\}$. These two combinations of homotopy types account for all pairs of opposite-handed trefoils, as a $\{2,3\}$ trefoil is ambient isotopic to a $\{3,2\}$ trefoil, *etc.*[19]

Consider an isotope containing only these pairs of gemini trefoils. It turns out that this graph topology is non-planar so it cannot be a polyhedral graph. The concept of graph planarity depends only on the graph topology rather than its embedding in space; a planar graph is one that can be drawn in the plane (or, equivalently, the sphere) without edge-crossings; a non-planar-graph cannot. Therefore, planar graphs can be realised by spherical isotopes whereas *all* isotopes of non-planar graphs require toroidal or higher genus embeddings. Non-planarity can be shown by considering the universal cover, in which the resulting graphs are (4,4) tilings of $\mathbb{E}^2$ *i.e.* containing four quadrilaterals around each vertex. Two relative orientations are possible, giving two distinct isotopes (embedded graphs): pairs of knots with homotopy types $\{2,3\}\otimes\{2,-3\}$ (isotope *A*) and $\{2,3\}\otimes\{3,-2\}$ (isotope *B*), illustrated in Fig. 3. (Other enantiomeric trefoil pairs are equivalent to one of these cases by symmetry.) These universal covers wrap onto the standard torus embedding in $\mathbb{E}^3$ to give achiral toroidal isotopes, shown in Fig. 4. But are they planar? (The wrapping process for isotope B from the universal cover to the embedded graph can be found in the ESI.†)

We can rule out the possibility of a graph being planar – and hence polyhedral – as follows. Suppose it is planar, in which case it can be drawn on a sphere, generating *F* faces from its *E* edges and *V* vertices. We can then apply Euler's Theorem to the reticulation.[14]

$$V - E + F = 2$$



(a) Isotope *A* (b) Isotope *B*

Fig. 4 Toroidal embeddings of the two gemini trefoil isotopes, corresponding to the universal covers shown in Fig. 3. The colours of vertices and edges are inherited from Fig. 3: each trefoil enantiomer is coloured by blue or brown edges.

Dividing by *F*, we have

$$\frac{n}{z} - \frac{n}{2} + 1 = \frac{2}{F}$$

where $\frac{V}{F} = \frac{n}{z}$ and $\frac{E}{F} = \frac{n}{2}$ and z, n denote the average degree of each vertex and the average polygonal (cycle) size of the faces in the spherical reticulation. These relations result since each vertex is shared between z faces, each edge between two faces and faces are polygons of size n.

Since each vertex in isotopes *A* and *B* has four neighbours, the degree of our graph is 4 ($z = 4$) and

$$n = 4 - \frac{8}{F}.$$

The faces must therefore obey the relation $n < 4$. Since this condition holds if the graph can be embedded on a topological sphere, a 2-manifold of positive Gaussian curvature, we call this for convenience the positive curvature condition.

Since neither of our isotopes with gemini pairs of trefoils contain cycles which can be found with less than four edges, they violate the positive curvature condition. Therefore neither of these achiral isotopes can be unknotted to form polyhedral graphs and they lie outside the class of graphs of interest, since the presence of trefoil enantiomers enforces non-planarity.

Now that the graphs of these gemini trefoil isotopes have been shown to be non-planar, we turn our attention to larger graphs, which contain these non-planar graphs within them as graph minors. This is done using Kuratowski's Theorem,[2,19,22] which adopts a different topological approach to the planarity of graphs. The theorem identifies essential features *not present* in *planar* graphs, which includes all polyhedral graphs. It states that any graph is non-planar if and only if it contains either the complete graph with five vertices (K_5) or the bipartite graph with six vertices ($K_{3,3}$) (or both) as a minor.

Since isotopes *A* and *B* have been shown above to possess insufficiently small cycles to reticulate $\mathbb{S}^2$, they are non-planar. By Kuratowski's Theorem,[22] they must both contain one of the 'forbidden' graphs as a minor. In fact, both *A* and *B* contain $K_{3,3}$ and K_5 as minors (see, *e.g.* Fig. 5). It is therefore certain that any graphs related to the *A* and *B* isotopes by appending extra edges and/or vertices are non-planar, since the forbidden graph minor remains intact. This proves that the

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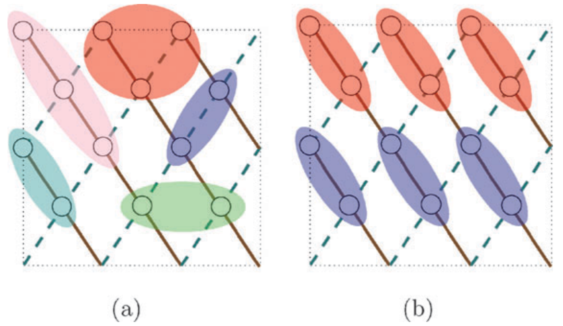

Fig. 5 (a) K_5 as a graph minor of an isotope A, shown in Fig. 3(a) and 4(a), in the universal cover. Vertices of K_5 formed by the edge-contraction and vertex-deletion of this 2-periodic graph are assigned distinct colours. (b) $K_{3,3}$ is also a minor of isotope A.

presence of a non-planar component induces non-planarity in the larger isotope. The same argument is used through the next two sections: the graphs containing just the enantiomeric knots or links is shown to be non-planar (and so non-polyhedral), a result which generalises to any isotope which contains them *via* this use of Kuratowski's theorem.

IV. Toroidal isotopes containing a $k\{p,q\}$ torus link

A similar argument to that presented in section III shows that all gemini pairs of torus knots and torus links containing chiral components also fail to be polyhedral graphs. Any isotope containing a torus link composed of k components of homotopy type $\{p,q\}$ (p and q co-prime), denoted $k\{p,q\}$, must also contain a gemini partner of type $k\{p,-q\}$ or $k\{-q,p\}$ in order to be achiral. We show below that all such isotopes share the characteristic of the gemini trefoil isotope, namely an absence of cycles traversing fewer than four edges. They are thus also prohibited from being polyhedral graphs since they are necessarily non-planar.

Since knots can be considered to be 'one-component links' we include their analysis by allowing k to equal one. We consider separately the isotopes generated by geodesics of the form $k\{p,q\} \otimes k\{p,-q\}$ and $k\{p,q\} \otimes k\{-q,p\}$.

A Graph generated by geodesics $k\{p,q\} \otimes k\{p,-q\}$

In the minimal isotope containing only the vertices and edges generated by $k\{p,q\} \otimes k\{p,-q\}$, consider the length of the smallest cycles involving each vertex. Viewed in the universal cover, these cycles are either nullhomotopic cycles of length four (since the faces in the torus and its universal cover are quadrilaterals) or else are paths linking translationally distinct copies of a vertex. (The face size is four, so a null-homotopic closed path must also be of length at least four edges.) The path from any vertex to its (α,β) translation is composed of M edges in the direction of (p,q) and N edges in the direction of $(p,-q)$. These vectors are $\frac{(p,\ q)}{2kpq}$ and $\frac{(p,\ -q)}{2kpq}$, *i.e.*

$$M\frac{(p,\ q)}{2kpq} + N\frac{(p,\ -q)}{2kpq} = (\alpha,\ \beta),$$

and *via* rearrangement

$$\left(\frac{M+N}{2kq}, \frac{M-N}{2kp}\right) = (\alpha,\ \beta),$$

so

$$(|M\ +\ N|, |M\ -\ N|)\ =\ 2k(|\alpha q|, |\beta p|).$$

Combining this equation with the triangle inequality gives both:

$$\begin{cases} |M| + |N| \geq |M + N| = 2k|\alpha q|, \\ |M| + |N| \geq |M - N| = 2k|\beta p|. \end{cases}$$

Thus

$$|M|\ +\ |N|\ \geq\ 2k\max(|\alpha q|, |\beta p|).$$

In the case of a pair of gemini knots, where $k\ =\ 1$, $|p|$ and $|q|$ are both at least 2 (to form a knot) and $(\alpha,\beta)\ \neq\ (0,0)$ so the number of edges traversed, $|M|\ +\ |N|$ is at least four. In the case of a link, where $k\ \geq\ 2$, $|p|$ and $|q|$ are both at least one (in order to be interlinked), and again $(\alpha,\beta)\ \neq\ (0,0)$ so the number of edges traversed, $|M|\ +\ |N|$ is also at least four. Thus there is no cycle in the isotope containing less than four edges. It follows that all isotopes which contain these specific gemini pairs violate the positive curvature condition hence they cannot be planar, and are not polyhedral graphs.

B Graph generated by geodesics $k\{p,q\} \otimes k\{-q,p\}$

Gemini pairs can also result from a minimal isotope containing only $k\{p,q\} \otimes k\{-q,p\}$. Again consider the path from any vertex to its (α,β) translation, composed of M edges in the direction of (p,q) and N edges in the direction of $(-q,p)$. These vectors are $\frac{(p,\ q)}{k(p^2+q^2)}$ and $\frac{(-q,\ p)}{k(p^2+q^2)}$. Thus

$$M\frac{(p,\ q)}{k(p^2+q^2)} + N\frac{(-q,\ p)}{k(p^2+q^2)} = (\alpha,\ \beta),$$

so

$$\frac{1}{k(p^2+q^2)}\begin{bmatrix} p & -q \\ q & p \end{bmatrix}\begin{bmatrix} M \\ N \end{bmatrix} = \begin{bmatrix} \alpha \\ \beta \end{bmatrix}.$$

Rearranging,

$$\begin{bmatrix} M \\ N \end{bmatrix} = k(p^2+q^2)\begin{bmatrix} \frac{p}{p^2+q^2} & \frac{q}{p^2+q^2} \\ \frac{-q}{p^2+q^2} & \frac{p}{p^2+q^2} \end{bmatrix}\begin{bmatrix} \alpha \\ \beta \end{bmatrix}.$$

Observing that the square matrix is a rotation matrix, and thus leaves vector length unchanged:

$$||(M,\ N)||\ =\ k(p^2\ +\ q^2)||(\alpha,\beta)||,$$

where $||(x,\ y)||$ denotes the length of the vector $(x,\ y)$. Now

$$|M| + |N| \geq \sqrt{|M|^2 + |N|^2} = \sqrt{M^2+N^2} = ||(M,\ N)||$$

Since $(\alpha,\beta)\ \neq\ (0,\ 0)$, $||(\alpha,\beta)||\ \geq 1$, so that

$$|M|\ +\ |N|\ \geq\ k(p^2\ +\ q^2)\ \geq\ 4$$

for all k, p and q under consideration. Thus there is no cycle in the isotope containing less than four edges, and any isotope which contains these gemini pairs violates the positive curvature constraint and is not a polyhedral graph.

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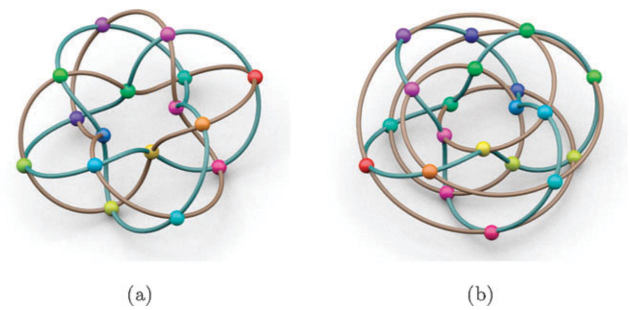

Fig. 6 Two isotopes, each built from a left- and a right- handed pair of Whitehead links, *i.e.* (a) $2\{1,2\} \otimes 2\{-1,2\}$ and (b) $2\{1,2\} \otimes 2\{-2,1\}$. Each chiral component is coloured either brown or blue in both isotopes. Their universal covers are shown in Fig. 7.

Consider, for example, an isotope with a gemini pair of Whitehead links (the unique two component link with five crossings), with homotopies $2\{1,2\} \otimes 2\{-1,2\}$ and $2\{1,2\} \otimes 2\{-2,1\}$, shown in Fig. 6, whose universal cover is shown in Fig. 7. The diagrams verify that even for these simple isotopes, no cycle shorter than length four exists, whether null-homotopic or of non-trivial homotopy.

V. Toroidal isotopes containing achiral Hopf links

Thus far, the construction of achiral toroidal graph embeddings involves gemini pairs of enantiomers, covering all examples of graphs with minors consisting of chiral knots or links on the torus. Just one achiral example of non-trivial toroidal knots or links exists: the Hopf link.

Suppose we have a polyhedral graph that contains no tangling more complex than a Hopf link, *i.e.* a pair of loops of homotopy type $(1, 1)$, *viz.* $\{2, 2\}$. Since the graph must be simple to be polyhedral, rather than a multigraph, it must contain at least six vertices (three per loop). Since it is also by definition 3-connected, it can be drawn as a twisted ladder, with at least three rungs (Fig. 9): any fewer rungs would allow splitting of the ladder into a pair of disconnected loops by removal of two vertices. However Simon has proven that a twisted ladder of this type is chiral provided the number of rungs exceeds two,[23] so embedded polyhedral graphs with a Hopf link as a minor must contain a chiral component. Recall that we are searching for achiral embeddings. To ensure an achiral isotope, we must either include a second twisted ladder enantiomeric to the first, as in Fig. 8, or alternatively add extra rungs to the Hopf link 'rails', giving both right- and left-handed twisted ladders as graph minors, as in Fig. 9. The first case can be readily dismissed since there is no cycle of length shorter than four in Fig. 8, null-homotopic or otherwise. It therefore violates the positive curvature condition and the underlying graph is non-planar, so the isotope is not polyhedral.

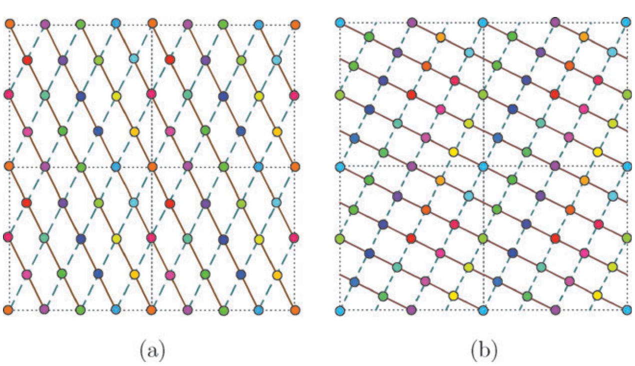

Fig. 7 A part of the universal covers of (a) $2\{1,2\} \otimes 2\{-1,2\}$ and (b) $2\{1,2\} \otimes 2\{-2,1\}$ isotopes, *i.e.* left- and right-handed Whitehead links. The shortest non-null-homotopic cycles are of lengths four and six, respectively (*e.g.* walks between similarly coloured vertices.). The link enantiomers are distinguished by the full (brown) and dashed (blue) lines.

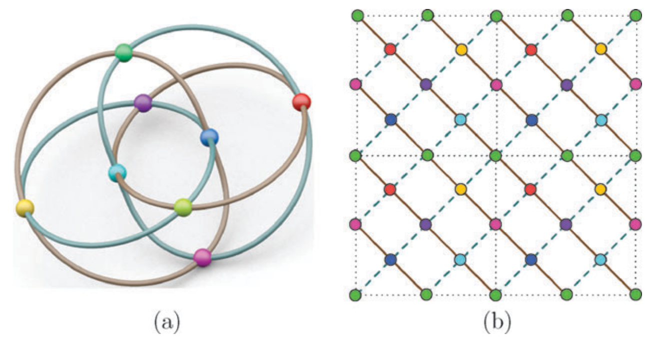

Fig. 8 (a) An isotope composed of two 'orthogonal' sets of Hopf links, with homotopies $2\{1,1\} \otimes 2\{1,-1\}$ shown in blue and brown, respectively. (b) A part of the universal cover of the isotope; each set of Hopf links is shown by blue (dashed) and brown (full) lines, with vertex colours corresponding to image (a). From either image it can be determined that there is no cycle shorter than length four, so any graph containing these elements is non-planar.

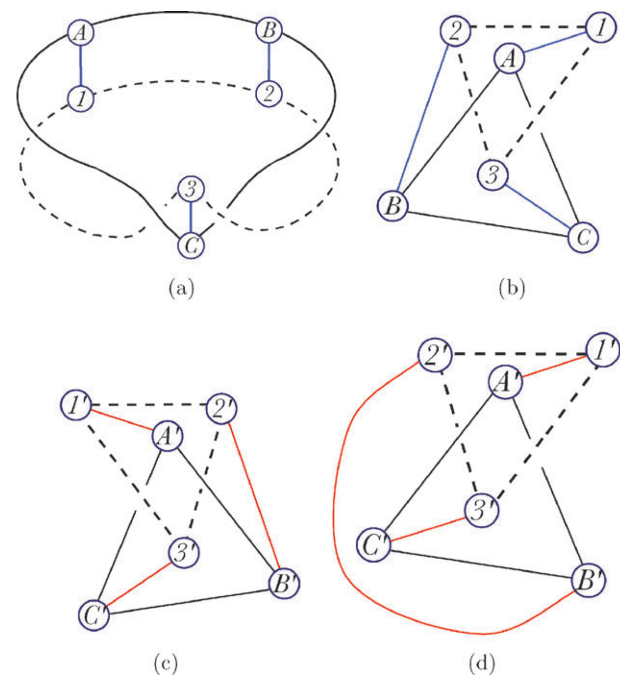

Fig. 9 (a) The simplest polyhedral graph embedding with a single Hopf link: the chiral three-rung twisted ladder (an isotope of the triangular prism). (b) Alternative embedding of the isotope in (a). (c) The three-rung ladder enantiomeric to (a) and (b). (d) Alternative embedding of isotope (c) with Hopf link presentation common to that of (b).

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The second possibility, consisting of an enantiomeric pair of twisted ladders contained on a single pair of Hopf link 'rails' – an inclusion which minimally requires one additional rung – can be addressed by considering the planar embedding of the graph of such an isotope. The chiral component of one hand must be drawn as two cycles joined by three rungs, as per Fig. 10. Since the graph is assumed to be planar, in this planar embedding the rungs must not cross, so assigning an arbitrary orientation to one component of the Hopf link induces an orientation in the other, through the rung connectivity.

Any reflection of this component (required to complete the gemini pair) interchanges the linking of these two oriented cycles, again defined by rung connectivity. However there is no way to interchange the orientation of one of these cycles without inducing rung crossings, even if the cycles themselves are interchanged, as shown in Fig. 10.

Thus any isotope which contains an enantiomeric pair of twisted ladders with at least three rungs on the same or different rails cannot have a planar embedding and cannot be a polyhedral graph. So even the presence of the simplest toroidal entanglement mode in an embedding of a polyhedral graph – a mere Hopf link – is sufficient to induce chirality in the resulting toroidal isotope.

VI. Conclusion

This work has been motivated by earlier enumerations of toroidal isotopes of the cube[17] and a more extensive enumeration of toroidal tetrahedral, cube and octahedral isotopes.[15] Here, we have explored the possibility of forming achiral embedded graphs on the torus ('toroidal isotopes') formed from *any* polyhedral graph. It turns out that all such achiral isotopes containing knots or links fail to be polyhedral graphs, as they are either nonplanar or not 3-connected. This finding is analogous to the simpler well-known result for knots and links on the torus: In those cases, all knots and links with more than three crossings are chiral. Here we have shown that *all* polyhedral (simple, planar, 3-connected) graphs that contain torus knots or links are chiral.

The result is valid for the most general form of ambient isotopic deformations of a graph – a class that may be broader than definitions admitted by chemical realisations of these graphs.[2] Kauffman introduced *rigid-vertex graphs*, whose ambient isotopic deformations preserve the edge ordering around a vertex in a local 2-manifold embedding.[20] It follows that all toroidal embeddings of planar, 3-connected rigid-vertex graphs are also chiral.

It is of interest in this context to deduce examples of toroidal isotopes that violate the requirements of polyhedral graphs, showing that the theorem cannot be broadened beyond polyhedral graphs. Recall that three features are essential to polyhedral graphs: they must be planar, three-connected and simple.

We have encountered many examples of 3-connected, simple graphs that form achiral toroidal isotopes, but have no planar embedding. An example is the enantiomeric pair of trefoils illustrated in Fig. 5.

Relaxing the 3-connectivity condition to 2-connectivity allows an 'almost polyhedral' graph with eight vertices of degree three, that embeds achirally on the torus to give a single Hopf link, shown in Fig. 11.

Examples of achiral 3-connected, planar *multigraphs* can be found whose minimal embedding is in the torus. A simple case is illustrated in Fig. 12. Like the previous example, this isotope contains a Hopf link. This achiral toroidal isotope is a sub-graph of the example in Fig. 11, retaining only the four vertices connecting distinct loops of the Hopf link. This isotope demonstrates the necessity of the condition of simplicity to induce chirality.

Lastly, note that it is easy to generate achiral examples of knotted polyhedral graphs by choosing 2D embeddings of multi-handled tori. For example, achiral examples of bitorus (genus 2) isotopes are generated by placing mirror images of knotted, chiral toroidal isotopes on each handle of the bitorus.

Note that our proof has considered all toroidal isotopes of polyhedral graphs containing knots and/or links. Certainly, any toroidal polyhedral graph must contain an entanglement of some kind, since otherwise it would reticulate the sphere rather than the torus. (Alternatively, we could use this minimal embedding constraint to define entangled polyhedral graphs.) We know, however, that entanglements can occur without the presence of knots or links, such as ravels, that tangle an isotope without entangling individual cycles.[21] The simplest ravels that we can construct embed in the genus-two bitorus. Other higher-order entanglements are also likely to occur; we doubt that any of these can form genus-one toroidal reticulations. We therefore conjecture that *all* toroidal isotopes are chiral.

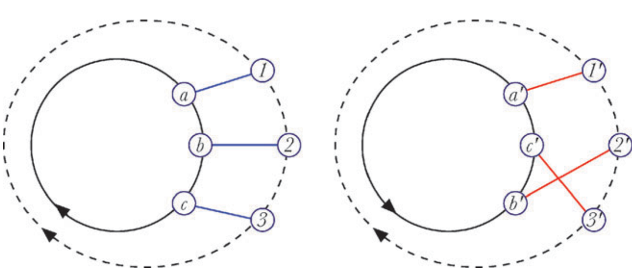

Fig. 10 The planar embedding of both handed three-rung twisted ladders shown in Fig. 9. For any orientation of the Hopf link 'rails', at least one of the left- or right-handed components must have an unremovable crossing.

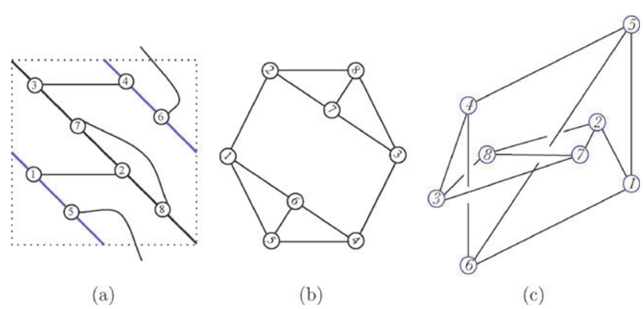

Fig. 11 (a) Universal cover of an 8-vertex, degree-3 achiral toroidal isotope of a (b) planar 2-connected graph. (c) An embedding of the isotope in $\mathbb{E}^3$ that contains a mirror plane (containing the square face 1546).

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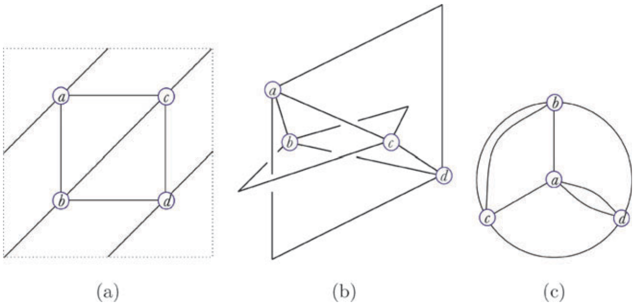

Fig. 12 (a) The universal cover of an achiral toroidal isotope of a (b) multigraph that is (c) planar and three-connected.

The implications of this result for chemistry are potentially profound. We give just two examples here. First, just as polymeric chains inevitably knot as their length grows in solution,[24] entangled structures are likely to emerge during synthesis of polyhedral graphs that contain extended graph edges, such as DNA complexes whose helices define the edges of polyhedra.[11] The 'simplest' entanglements, assembled most readily apart from the conventional (untangled) polyhedral forms are likely to be toroidal; it is therefore of interest to note that these structures are chiral (in addition to possible chirality induced by the individual DNA strands). Second, many carcerands can be represented as polyhedral graphs (provided they are three-connected and simple), since they typically surround a central guest species and are therefore topologically planar. Synthesis of these molecules *via* templating on a substrate that it topologically toroidal, such as any simple unicyclic molecule, will then induce an entangled carcerand that is necessarily topologically chiral. Conversely, polyhedral host structures that encapsulate annular or toroidal guests are necessarily chiral.

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