J Math Chem (2015) 53:2078–2094
DOI 10.1007/s10910-015-0535-1

ORIGINAL PAPER

# On the existence of nanojoins with given parameters

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Received: 26 March 2015 / Accepted: 13 July 2015 / Published online: 28 July 2015


**Abstract** Nanojoins are parts of large carbon molecules joining several nanotubes with the same or different parameters and chemical and electrical properties. It is known that Euler's formula implies that such nanojoins must contain faces that are not hexagons if at least three tubes are joined. As the atoms in a nanojoin are carbon atoms preferring hexagonal rings, it is normally assumed that apart from hexagons only pentagons and heptagons occur. In this paper we will give necessary and sufficient conditions for the existence of nanojoins joining nanotubes with given parameters and given numbers of pentagons and heptagons.

**Keywords** Fullerene · Nanotube · Nanojoin

## 1 Introduction

In 1991 Iijima [12] reported the preparation of graphitic carbon needle-like tubes with diameter from 4 to 30 nm and up to 1 μm long. These needles were made up of coaxial carbon tubes, carbon nanotubes, in which the carbon atoms were arranged

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in hexagons. Carbon nanotubes have many potential applications and large quantities can be produced by various means [11,14].

Guo [10] reports on methods for the generation of nanojunctions between nanotubes. That is, there are various methods for joining nanotubes with the same or different diameters and properties. It is nanojoins, the structures that join the nanotubes together, that are of interest in this paper.

Iijima et al. [13] discuss the growth of nanostructures in which there are some pentagonal or heptagonal rings of carbon, and the effects of these polygons on the shape of these nanostructures.

Nanotubes and nanojoins can be represented as graphs in which carbon atoms are represented by vertices. Graph theory can be used to gain information about such structures and to enumerate them. For example, see [3–5]. This paper is concerned with graphs which represent nanojoins.

As the vertices in our graphs correspond to carbon atoms, non-hexagonal faces are especially relevant as they represent a deviation from the preferred ring size causing stress and leading to energetically less favourable structures. Furthermore, the tubes always contain many hexagons and the boundary between a tube and a nanojoin is of a purely artificial nature so that the question "How many hexagons must be present in a join?" does not make sense, while, no matter how the boundary between the join and the tube is defined, pentagons and heptagons must always be considered as part of the join.

In this paper we will give a full answer to the question of whether, for a given set of tubes with given parameters and given numbers $p$ of pentagons and $s$ of heptagons, a nanojoin with $p$ pentagons, $s$ heptagons and some number of hexagons exists that can join the given tubes.

## 2 Terminology

All graphs considered in this paper are connected plane graphs, that is, graphs embedded in the plane with a well defined cyclic order of edges around each vertex.

**Definition 1** The *degree sequence* of a face with edges $v_0v_1, v_1v_2, \ldots, v_nv_0$ in clockwise order around the boundary (seen from inside the face) is the cyclic series $\deg v_0, \deg v_1, \ldots, \deg v_n$.

In the literature the term *nanotube* is used for two kinds of structure. In [7] Dresselhaus describes it as "consisting of a planar honeycomb network of carbon atoms on a graphite sheet one atom thick and rolled up into a cylinder". The other structure is a tube shaped fullerene, that is, a plane graph with all vertices of degree 3 and all faces pentagons or hexagons in which the (necessarily) 12 pentagons come in two groups of 6 pentagons each, together with some hexagons close to them forming the *nanocaps*, connected by a finite part of a nanotube in the sense of Dresselhaus. The term *halftube* denotes one part of a nanotube (in the sense of Dresselhaus) that has been cut so as to produce two infinite parts, possibly capped at the cut with a nanocap. In this article tube and halftube will always refer to the non-capped versions.

Take an infinite plane graph in which all vertices have degree 3 and where all faces are hexagons except for a finite number of pentagons and heptagons. If there exists a finite 2-connected induced subgraph so that after its removal the components that remain are $k \geq 2$ halftubes, this substructure is called a *nanojoin* (joining these halftubes).

The structure of a tube or halftube can be described by 2 parameters (see [9]), often denoted as $l, m$. A nanotube with parameters $l, m$ has a closed path so that when cut along that path a face with degree sequence $(3, 2)^l, (2, 3)^m$ is created. Such paths are used to describe the border between a cap and the tube of a nanotube fullerene and also between the nanojoin and the tubes that are joined by it.

So in a nanojoin, seen as an isolated structure and not as a substructure, there are two kinds of faces: faces that are also faces in the whole, infinite, structure and *special* faces that come from cutting the tubes. This motivates the following definitions:

**Definition 2** • For each graph $G$ there is a (possibly empty) set $S(G)$ of faces. Faces $f \in S(G)$ are called *special faces*. If $f \in S(G)$ has degree sequence $(3, 2)^l, (2, 3)^m$ for some ($l > 0$, $m \geq 0$, $l + m \geq 2$) we call $f$ a *special t-face*.

- A *patch* is a (finite) graph $G$ with all faces $f \notin S(G)$ pent- hex- or heptagons and with all vertices of degree 2 or 3. The vertices with degree 2 are in the boundary of a special face. When there is only one special face, that face may be called the outer face.
- For a special face $S$ write $t = t(S)$ and $d = d(S)$ for the number of vertices of degree 2, respectively 3, in $S$. For a patch $P$ with only one special face $S$, write $t(P)$ for $t(S)$ and $d(P)$ for $d(S)$.
- A halftube is an infinite graph with one special t-face $f$ and all other faces hexagons, in which all vertices not in the special face have degree 3. If the degree sequence of $f$ is $(3, 2)^l, (2, 3)^m$ for some $l$ and $m$, we say that the halftube has parameters $(l, m)$.
- A *nanojoin* is a patch in which all $k \geq 2$ special faces are special t-faces.

Assume that we have a special face $f_G$ with boundary $v_1v_2, v_2v_3, \ldots, v_{2(l+m)}v_1$ giving the degree sequence $(3, 2)^l, (2, 3)^m$ and a halftube with special face $f_H$ formed by the edges $w_1w_2, w_2w_3, \ldots, w_{2(l+m)}w_1$ giving the same degree sequence. Looking at the boundary of $f_H$ in anticlockwise order and starting with $w_{2l}$, that is, $w_{2l}w_{2l-1}, \ldots, w_1w_{2(l+m)}, \ldots w_{2l+1}w_{2l}$, we get a sequence of degrees that is $(2, 3)^l, (3, 2)^m$. Identifying $v_1$ with $w_{2l}$, $v_2$ with $w_{2l-1}, \ldots,$ and finally $v_{2(l+m)}$ with $w_{2l+1}$ the identified vertices $v_i$ and $w_j$ all have the property that $\deg v_i + \deg w_j = 5$. As the two edges in the boundaries of the special faces are the same after identification, the result is that all identified vertices have degree 3 and the two special faces have been deleted. This operation models the gluing of a halftube to the special face of a nanojoin with the same parameters. Applying such a procedure to each special t-face of a nanojoin shows that the structures defined as nanojoins can in fact be obtained by the cutting operation informally described before Definition 2 and that a nanojoin can be used to join together halftubes with the same or different parameters corresponding to the special faces. We will use the same kind of operation to identify boundaries of special faces of nanojoins.

## 3 Preliminary results

**Proposition 3.1** *If a nanojoin joining k halftubes has p pentagons and s heptagons, then* $s = p + 6(k - 2)$. *In particular, a nanojoin joining* 2 *halftubes has the same number of pentagons as heptagons.*

*Proof* Consider a nanojoin with $k$ special faces, $h$ hexagons, $p$ pentagons and $s$ heptagons and with the degree sequences of the special faces $(3, 2)^{l_i}, (2, 3)^{m_i}$ for $i = 1, \dots, k$. Counting the numbers of edges (or equivalently vertices), face by face, we count each edge twice and, except for the vertices of degree 2 in the boundary of the special faces, each vertex 3 times. In a special face with parameters $(l, m)$ there are $l + m$ vertices of degree 2. This gives us the following formulas for the number of faces $|F|$, edges $|E|$ and vertices $|V|$:

$$|F| = h + p + s + k$$

$$2|E| = 6h + 5p + 7s + 2\sum_{i=1}^{k}(l_i + m_i)$$

$$3|V| = 6h + 5p + 7s + 3\sum_{i=1}^{k}(l_i + m_i) = 2|E| + \sum_{i=1}^{k}(l_i + m_i).$$

Inserting these into Euler's Formula, $6|V| - 6|E| + 6|F| = 12$, one obtains $s = p + 6(k - 2)$. □

**Lemma 3.2** *Consider a patch* $P$ *with one special face* $S$, $p$ *pentagons and* $s$ *heptagons. Let* $t = t(S)$ *and* $d = d(S)$. *Then* $p - s = 6 - (t - d)$.

*Proof* Let $h$ be the number of hexagons in the patch. The number of faces $|F|$, edges $|E|$ and vertices $|V|$ are given by $|F| = p + h + s + 1$, $2|E| = 5p + 6h + 7s + t + d$ and $3|V| = 2|E| + t$.

Using Euler's Formula we obtain $p - s = 6 - (t - d)$. □

In order to be able to refer to it, we give the following Lemma, but without the easy proof.

**Lemma 3.3** *Let the path* $v_1v_2, v_2v_3, \dots, v_{k-1}v_k$ *be part of a special t-face and* $s$ *be the corresponding sequence of degrees. Let* $t(s)$ *and* $d(s)$ *be the number of twos, respectively threes, in* $s$. *Then* $t(s) - d(s) \leq 2$.

## 4 Nanojoins joining two halftubes

In this section we will give necessary and sufficient conditions for the existence of nanojoins containing $p$ pentagons and $s$ heptagons that join two halftubes with parameters $(a, b)$ and $(c, d)$. While the existence proofs will all be given in this section, a non-existence proof for one case will be postponed until the end of the article.

**Theorem 4.1** *There exist nanojoins with* $p$ *pentagons and* $s$ *heptagons joining two halftubes with parameters* $(a, b)$ *and* $(c, d)$ *if and only if* $a + b \geq 2,\ c + d \geq 2$ *and*

- $p = s = 0$ *and* $(a, b) = (c, d)$*;*
- *or* $p = s = 1$ *and* $(a, b) \neq (c, d)$*;*
- *or* $p = s \geq 2$.

The conditions $a + b \geq 2$ and $c + d \geq 2$ are necessary for the existence of halftubes (otherwise there would be double edges). For $a + b \geq 2,\ c + d \geq 2$ the existence of halftubes can easily be seen using the construction described by Dresselhaus [8].

It has been known for many years that nanojoins with $p = s = 0$ join halftubes with $(a, b) = (c, d)$. This just rephrases the well definedness of the parameters for nanotubes.

We will need some lemmas/basic facts before giving the proof of the theorem.

**Lemma 4.2** *If* $(a, b) \neq (c, d)$ *and* $a + b \geq 2,\ c + d \geq 2$*, there exists a nanojoin with* $p = s = 1$ *joining two halftubes with parameters* $(a, b)$ *and* $(c, d)$.

*Proof* We may assume that $a + b \geq c + d$. Start with a ring of hexagons having boundary sequence $(a, b)$ on both sides. Add a ring consisting of one pentagon and $a + b - 1$ hexagons to this nanojoin. If $b \neq 0$ place the pentagon where there are two adjacent vertices of degree 2. The nanojoin has become a patch with one special face a special t-face with parameters $(a, b)$ and a second special face having degree sequence $3, (3, 2)^{a+b-1}$. With each ring of hexagons added to the boundary of the second special face, we get a new boundary where the exponent is 1 smaller, so by adding rings of hexagons we can obtain a patch whose outer face has degree sequence $3, (3, 2)^{c+d-1}$.

Give label 0 to the face with two adjacent vertices of degree 3 in the outer ring, then label the faces in the outer ring consecutively in clockwise order seen from the special face. Replace the face labeled $c$ by a heptagon. Since $(c, d) \neq (a, b)$, this face is not the pentagon, no matter whether hexagon rings have been added or not. The result is a special face with degree sequence $(c, d)$. See Fig. 1 for an example. □

Using this result, we can easily prove the third part in Theorem 4.1, which we will rephrase in the following lemma:

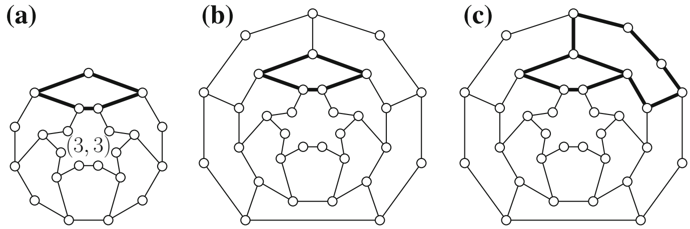



**Fig. 1** **a** Add a ring with one pentagon to a (3, 3) nanocap, **b** add a ring of hexagons, **c** replace a hexagon by a heptagon to obtain a special face with degree sequence $(3, 2)^2(2, 3)^3$

**Lemma 4.3** *For each $n \geq 2$ and parameters $(a, b)$, $(c, d)$ with $a+b \geq 2$, $c+d \geq 2$ there exist nanojoins with $n$ pentagons and $n$ heptagons joining two halftubes with parameters $(a, b)$, respectively $(c, d)$.*

*Proof* For $n = 2$ choose parameters $(e, f) \neq (a, b), (c, d)$. By Lemma 4.2 there is a nanojoin for $(a, b)$ and $(e, f)$ with 1 pentagon and 1 heptagon. There is also a nanojoin for $(e, f)$ and $(c, d)$ with 1 pentagon and 1 heptagon. Identifying the nanojoins along the $(e, f)$ boundary gives a nanojoin for $(a, b)$ and $(c, d)$ with 2 pentagons and 2 heptagons.

Applying the same technique inductively, nanojoins with $n > 2$ pentagons and heptagons can be constructed. □

To complete the proof of Theorem 4.1 it remains to be shown that for $p = s = 1$ there is no nanojoin that can join two halftubes with the same parameters. From the chemical point of view this is possibly the least interesting case as for the same parameters an energetically much better join with only hexagons is possible. From the mathematical point of view, it is of course interesting to also decide this last case. As we will see, this case is by far the most difficult, so we postpone it to the last section.

## 5 Nanojoins joining three or more halftubes

**Theorem 5.1** *There exist nanojoins with $p$ pentagons and $s$ heptagons joining $k \geq 3$ halftubes with parameters $(l_i, m_i)$, $l_i + m_i \geq 2$, $1 \leq i \leq k$ if and only if $s = 6(k-2) + p$.*

Proposition 3.1 implies that $s = 6(k-2) + p$ is a necessary condition. What remains to be shown is that it is sufficient. Again we will prove the result with the help of some lemmas. We begin with joins joining 3 halftubes.

**Lemma 5.2** *Consider three parameters $(l_1, m_1)$, $(l_2, m_2)$ and $(l_3, m_3)$ with $l_i + m_i \geq 2$, $1 \leq i \leq 3$. There exists a nanojoin for three halftubes with parameters $(l_1, m_1)$, $(l_2, m_2)$ and $(l_3, m_3)$ with 6 heptagons and no pentagons.*

*Proof* Let $h$ be a hexagon in the hexagonal lattice and for $i \geq 0$ define the patch $P_i$ as the subgraph induced by all hexagons at distance at most $i$ from $h$ (with *distance* referring to the usual graph theoretic distance in the dual). The graphs $P_0$ and $P_1$ are depicted in Fig. 2. Define a side of $P_i$ to be a path in the (special) outer face with

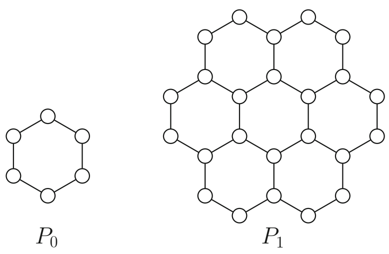



**Fig. 2** The graphs $P_0$ and $P_1$

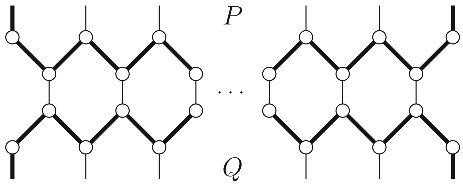



**Fig. 3** Connecting a side of $P$ to a side of $Q$

degree sequence $(2,3)^i, 2$. There are 6 sides, with $2i+1$ vertices each, and the union of these 6 sets of vertices is the vertex set of the special face of $P_i$.

Let $c = \max\{l_1+m_1, l_2+m_2, l_3+m_3, 6\}$, $k = \lfloor \frac{1}{2}c \rfloor - 1$ and let $P$ and $Q$ be copies of $P_k$. Let $S_1, \ldots, S_6$ be the sides of $P$ in clockwise order and $T_1, \ldots, T_6$ the sides of $Q$ in anticlockwise order. Connecting $S_1$ with $T_1$, $S_3$ with $T_3$ and $S_5$ with $T_5$ by adding an edge between corresponding vertices of degree 2 (see Fig. 3) we obtain a patch with 3 special faces. The degree sequence of each special face is $3, (2,3)^{k+1}, 3, (2,3)^{k+1}$.

Replacing, in each special face, one hexagon containing a boundary edge with two vertices of degree 3 by a heptagon changes the degree sequence of the special face to $3, (2,3)^{2k+3}$. Note that as $k \geq 2$ this procedure in fact replaces 3 different hexagons.

Adding $j$ rings of hexagons to the boundary of a special face yields a new special face with degree sequence $3, (2,3)^{2k+3-j}$. We successively add rings to special face number $i$, $1 \leq i \leq 3$, until the boundary has degree sequence $3, (2,3)^{l_i+m_i-1}$. Note that we add at least one ring of hexagons for each special face. A hexagon can then be replaced by a heptagon to insert a vertex of degree 2 in the correct position to obtain $(3,2)^{l_i}(2,3)^{m_i}$.

Having applied this method to each special face we have a nanojoin that joins 3 halftubes with parameters $(l_1, m_1)$, $(l_2, m_2)$ and $(l_3, m_3)$. □

**Lemma 5.3** *For $k > 2$ and parameters $(l_1, m_1), \ldots, (l_k, m_k)$, $l_i + m_i \geq 2$, $1 \leq i \leq k$, there exist nanojoins with no pentagons and $6(k-2)$ heptagons joining $k$ halftubes with the given parameter sets.*

*Proof* For $k = 3$ this is just Lemma 5.2. For $k \geq 4$ the result can then be proven by induction: assume $k$ parameters $(l_1, m_1), \ldots, (l_k, m_k)$ are given. By induction there exist two nanojoins where the special faces have parameters $(l_1, m_1), \ldots, (l_{k-1}, m_{k-1})$, respectively $(l_{k-1}, m_{k-1}), (l_{k-1}, m_{k-1}), (l_k, m_k)$. Identifying these nanojoins along the boundary of a special face with parameters $(l_{k-1}, m_{k-1})$, the resulting nanojoin has $k$ special faces with the required parameters and $6(k-3)+6 = 6(k-2)$ heptagons. □

There is one last step necessary to prove Theorem 5.1:

**Lemma 5.4** *For $k > 2$, $p \geq 0$ and parameters $(l_1, m_1), \ldots, (l_k, m_k)$, $l_i + m_i \geq 2$, $1 \leq i \leq k$, there exist nanojoins with $p$ pentagons and $6(k-2)+p$ heptagons joining $k$ halftubes with the given parameter sets.*

*Proof* For $p = 0$ this is just a reformulation of Lemma 5.3. By induction there exists a nanojoin with $p-1$ pentagons, $6(k-2)+p-1$ heptagons and special faces with parameters $(l_1, m_1), \ldots, (l_k + 1, m_k + 1)$. By Lemma 4.2 there also exists a nanojoin with 1 pentagon, 1 heptagon and 2 special faces with parameters $(l_k + 1, m_k + 1), (l_k, m_k)$. Identifying these joins along the boundary of a special face with parameters $(l_k + 1, m_k + 1)$, a nanojoin with the required special faces, $p$ pentagons and $6(k - 2) + p$ heptagons is obtained. □

## 6 The nonexistence of a nanojoin

The aim of this section is to prove that there is no nanojoin for two $(l, m)$ nanotubes which contains just 1 pentagon and 1 heptagon.

**Definition 3** A symmetric 5–7 nanojoin is a nanojoin for two nanotubes with the same parameters $(l, m)$ containing exactly 1 pentagon and 1 heptagon.

If $l \neq 0$ and $m \neq 0$ we call the edge where both endpoints have degree 3 the concave edge of the special face and the edge with two vertices of degree 2 the convex edge. Note that a special face has a concave edge if and only if it has a convex one and that it can have at most one edge of each type.

**Lemma 6.1** *In a symmetric* 5–7 *nanojoin the intersection of each non-special face $f$ with a special face $S$ is connected.*

*Proof* If $S \cap f$ has two or more components, we can remove the edges in $S \cap f$. This disconnects the nanojoin into (at least) two patches, one of which, say $P$, does not contain the other special face. The boundary sequence of $P$ is a subsequence $s_1$ of $S$ plus a sequence $2, 3^i, 2$ for some $i \geq 0$. By Lemma 3.3 we have that $t(s_1) - d(s_1) \leq 2$, with $t(s_1)$, $d(s_1)$ the numbers of twos, respectively threes, in $s_1$. For $P$ this implies $t(P) - d(P) \leq 4$ in contradiction to Lemma 3.2, which gives $t(P) - d(P) \geq 5$. □

A consequence of Lemma 6.1 is that a non-special face contains at most 2 vertices of degree 2 of each special face in a symmetric 5–7 nanojoin.

**Lemma 6.2** *Let $S$ be a special face of a symmetric* 5–7 *nanojoin. If two faces which intersect $S$ have a common edge, one of the vertices of that edge lies in $S$ or both faces share an edge with a pentagon at the convex edge of $S$.*

*Proof* Assume that the faces $f_1$ and $f_2$ intersect $S$ and have an edge in common with each other which does not contain a vertex of $S$.

Remove the edges in $f_1 \cap f_2$ and $S \cap (f_1 \cup f_2)$. This disconnects the nanojoin into (at least) two patches, one of which, say $P$, does not contain the other special face. The boundary sequence of $P$ is a subsequence $s_1$ of $S$ plus a sequence $2, 3^i, 2, 3^j, 2$ for some $i, j \geq 0$. If one of $i, j$ is larger than 0 we have $t(P) - d(P) \leq 4$, in contradiction to Lemma 3.2, so assume $i = j = 0$. This means that both edges of $P \cap S$ sharing a vertex with $f_1, f_2$ belong to the same face $\bar{f}$ in $P$ and due to Lemma 6.1 must be all of $P$. But if $\bar{f}$ is a hexagon or heptagon, the vertices not in $P \cap (f_1 \cup f_2)$ yield 2, 2, 2, respectively 2, 2, 2, 2 as a subsequence in the boundary of $S$, a contradiction, and if $\bar{f}$ is a pentagon, the vertices not in $P \cap (f_1 \cup f_2)$ yield 2, 2 as a subsequence—so the pentagon is at the convex edge. □

The key idea of the proof is to use a result by Dress [6] that there is no local disorder of the hexagonal lattice by 1 pentagon and 1 heptagon only. The mathematical basis of this approach was worked out in detail in [2] and later published as a complete classification result in [1].

An equivalent reformulation of this result is:

**Theorem 6.3** [6] *There is no patch (in the sense of Definition 2) with exactly* 1 *pentagon,* 1 *heptagon and* 1 *special face where the boundary of the special face describes a simple closed path in the hexagonal plane.*

We prove that a symmetric 5–7 nanojoin can be cut open in a way that the resulting patch contradicts Theorem 6.3.

The properties of the path along which we want to cut the symmetric 5–7 nanojoin are given in the following definition:

**Definition 4** Let $N$ be a symmetric 5–7 nanojoin with special faces with boundary sequence $(3, 2)^l(2, 3)^m$.

If a path has a start- or end-point in a degree 3 vertex of a special face, we say that it starts, respectively ends, in the $l$-part if the vertex is one of the vertices in the subsequence $(3, 2)^l$ (and analogously for the $m$-part).

A legal cutpath $p$ in $N$ is a path starting in one special face and going to the other with the following properties:

- (i) Either $l = 0$ or $m = 0$ or the start- and end-vertex of $p$ are in the same parts of their boundaries, that is, both are in the $l$-part or both are in the $m$-part.
- (ii) The path $p$ has as many right turns as left turns.
- (iii) Describing the path as a sequence $d_0, \ldots, d_k$ of right and left turns, for no subsequence $d_0, \ldots, d_i$, $i \leq k$, is the excess of right turns over left turns (or the other way around) more than 2. This implies that following the right and left turns in the hexagonal lattice, $p$ corresponds to a simple path.

**Theorem 6.4** *There is no symmetric* 5–7 *nanojoin with a legal cutpath.*

*Proof* Assume that there is a symmetric 5–7 nanojoin for parameters $(l, m)$ with a legal cutpath.

Note that for $l, m \neq 0$, the description of the boundary of the special face as a sequence of right and left turns starting at a vertex of degree three depends on the starting vertex. Nevertheless, for two sequences of right and left turns both obtained by starting in the $l$-part, respectively $m$-part, following the sequence of right and left turns starting at an edge in the hexagonal lattice will always give the same final edge in the lattice. If one of the parameters is 0, we get the same sequence of right and left turns independent of the starting point.

Cutting the resulting nanojoin along the legal cutpath we get a patch $S$ with one special face. The boundary of $S$ forms a closed curve in the hexagonal plane. This can be either proven by explicitly computing the coordinates of the start- and end-points or by observing that connecting the endpoints of the four subpaths that constitute the boundary (that is, the two paths coming from the special faces and the two paths coming from the cut) yield a parallelogram.

If this boundary path of $S$ in the lattice is not simple, the properties of the four subpaths (in particular, that they are simple) allow the addition of hexagons to $S$ so that the resulting patch has a simple boundary and therefore contradicts Theorem 6.3.

To see this, add patches from the hexagonal grid. If, for example, a part $a$ of the boundary intersects other parts of the boundary and is directed so that it has the nanojoin on its right side, we can choose a simple path $p$ in the hexagonal lattice connecting the start edge with the end edge of $a$ and otherwise not intersecting the closed curve. This can be done so that the interior of the simple closed curve formed by $p$ and $a$ is on the left side of $a$. Adding all hexagons inside the simple closed curve formed by $p$ and $a$, in the resulting patch the boundary cycle has fewer intersections. □

Now we want to prove that any symmetric 5–7 nanojoin has a legal cutpath, and therefore does not exist. If a non-special face contains a convex edge and a concave edge, these must belong to different special faces and there is one edge connecting the two special faces. This edge forms a legal cutpath, so that we have the following lemma:

**Lemma 6.5** *There is no symmetric* 5–7 *nanojoin with a face carrying a convex and a concave edge.*

**Definition 5** A thin path in a symmetric 5–7 nanojoin $N$ is a maximal set of connected faces that have edges in more than one special face. An interior face of a thin path is a face that has 2 neighbours in the path.

We will first show that a thin path is in fact a path (in the dual) and not a cycle.

**Lemma 6.6** *A thin path in a symmetric* 5–7 *nanojoin corresponds to a path in the dual.*

*Proof* If a face in the thin path neighbours three or more other faces in the thin path, one can easily construct a contradiction to the Jordan Curve Theorem, so each face neighbours at most two other faces in the set and the corresponding subgraph in the dual is a path or a cycle.

If the thin path is a cycle, then it would be the whole nanojoin and the heptagon would be at a convex edge of the special face $S$ (so $l, m \neq 0$). The convex edge of the other special face $S'$ would be at a hexagon, which would then also carry the concave edge of $S$, contradicting Lemma 6.5. □

**Lemma 6.7** *Suppose there is a pentagon or hexagon $f$ at the end of a thin path of a symmetric* 5–7 *nanojoin.*

*If $f$ is a hexagon, it contains at least one concave edge of a special face. If $f$ is a pentagon, then it contains the concave edges of both special faces.*

*If $f$ is the only element of the thin path, then $f$ is a hexagon and contains the concave edges of both special faces.*

*Proof* The fact that $f$ is an endpoint of a thin path implies that a neighbouring face shares edges with only one special face and as special faces do not share a vertex, at least 3 of the edges of $f$ are not contained in a special face and at most 3 are contained in a special face. So at least one of the intersections of a hexagon with a special face contains only one edge, which must have consecutive vertices of degree 3 at its ends. For a pentagon, both intersections must have this property.

If $f$ is the only element of the thin path, at least 4 of the edges of $f$ are not contained in a special face. So $f$ cannot be a pentagon and, as we assume it is not a heptagon, must be a hexagon and each intersection with a special face consists of a single edge. □

**Lemma 6.8** *A thin path p in a symmetric* 5–7 *nanojoin N has the following properties:*

(i) *p does not contain a face with a convex edge.*
(ii) *p has a concave edge but does not contain two concave edges.*
(iii) *p does not contain interior faces that have a concave edge.*
(iv) *p does not contain a pentagon in the interior.*
(v) *p has a heptagon at one end.*

*Proof* We will call an edge with endpoints in both special faces a crossing edge.

(i) Except for a heptagon in the interior of a thin path, each face with a convex edge would also have the concave edge of the other face—contradicting Lemma 6.5. If a heptagon in the interior of a thin path carries a convex edge, due to Lemma 6.7 the path has concave edges at both ends. In this case the crossing edge of the heptagon that lies on the same side of the heptagon as the concave edge of the special face with the convex edge is a legal cutpath. This contradicts Theorem 6.4.
(ii) If there is no concave edge, each face in $p$ has at least two edges in each special face. A face $f$ at the end of $p$ shares also at least 3 edges with neighbours in $N$. So $f$ must be a heptagon. As there is only one heptagon, this must be the only element of $p$, but then $f$ would share at least 4 edges with $N$—a contradiction. If the thin path contains two different faces with a concave edge, due to (i) any crossing edge between these two faces would be a legal cutpath, contradicting Theorem 6.4. If the thin path contains only one face carrying both concave edges, this face is a hexagon or heptagon and the only face in the thin path. Add a hexagon to the concave edge of one of the special faces $S$, then continue along $S$ in one direction, adding hexagons until the edge before the convex edge of $S$. This is illustrated in Fig. 4. This produces a symmetric 5–7 nanojoin with the same parameters and a legal cutpath is obtained, contradicting Theorem 6.4.

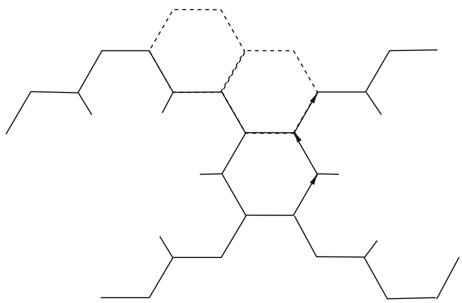


**Fig. 4** Adding faces to a join with a thin path containing exactly one hexagon and the resulting legal cutpath

(iii) Due to Lemma 6.7 at least one of the endpoints would contain a concave edge too, in contradiction to (ii).
(iv) A pentagon in the interior of a thin path would have a concave edge, contradicting (iii).
(v) This follows directly from (ii) and Lemma 6.7. □

**Definition 6** For a special face $S$ of a nanojoin $N$ with parameters $l, m \neq 0$, a convex-to-concave path (cc-path for short) is a set of faces containing the face carrying the convex edge and all faces in one of the two directions until, but not including, the face carrying the concave edge. If all these faces are hexagons and have edges in just one special face, we call the cc-path a simple cc-path.

The graph with the cc-path $r$ removed is the graph induced by the vertices from $N$ that do not lie in $S \cap r$.

Lemmas 6.1 and 6.2 imply that the name path is not misleading. Unless the path consists of a single face, each face in the path neighbours exactly two other faces in the path except for the endpoints that only neighbour one.

**Lemma 6.9** *Let $N$ be a symmetric* 5–7 *nanojoin with a special face $S$ and a simple cc-path. By removing this simple cc-path a nanojoin with the same parameters is obtained.*

The degree sequence of the new special face can easily be seen to be the same as that of the original special face.

Using Lemma 6.9 we may recursively delete each simple cc-path from a symmetric 5–7 nanojoin.

**Definition 7** A symmetric 5–7 nanojoin without simple cc-paths is called a reduced symmetric 5–7 nanojoin.

We obtain the next Lemma.

**Lemma 6.10** *If there exists a symmetric* 5–7 *nanojoin for nanocaps with parameters* $(l, m)$ $(l, m \neq 0)$ *there also exists a reduced symmetric* 5–7 *nanojoin with the same parameters* $(l, m)$.

*In a reduced symmetric* 5–7 *nanojoin $N$ with parameters* $(l, m)$ $(l, m \neq 0)$ *there is no thin path and the heptagon contains a convex edge.*

*Proof* By removing simple cc-paths we obtain a reduced symmetric 5-7 nanojoin with the same parameters.

If $N$ contains a thin path, this path has a heptagon at one end (Lemma 6.8). Each special face has one cc-path not containing faces of the thin path, as a concave edge cannot be in the interior of a thin path (Lemma 6.8). So none of these cc-paths contains the heptagon and only one can contain the pentagon, which implies that at least one cc-path is simple, which is a contradiction to the nanojoin being reduced.

So $N$ does not contain a thin path. If the heptagon does not contain a convex edge, at least one of the convex edges is contained in a hexagon. At this hexagon two cc-paths start that only share the hexagon. As $N$ does not contain a simple cc-path, one cc-path must contain a heptagon and one a pentagon. This implies that the convex edge of the other special face is also contained in a hexagon and that both cc-paths starting there are simple, a contradiction to $N$ being reduced. □

This gives us the following result:

**Lemma 6.11** *If there exists a symmetric* 5–7 *nanojoin $N$ for parameters $(l, m)$, there also exists a symmetric* 5–7*nanojoin with parameters $(l, m)$ with a heptagon at the boundary of a special face and if $l, m \neq 0$ the heptagon is at the convex edge.*

*Proof* For $l, m \neq 0$ this is just a reformulation of Lemma 6.10. For $l = 0$ or $m = 0$, Lemma 6.8(ii) implies that $N$ does not have a thin path, so we have one special face that does not have the pentagon in the boundary and we can remove rings of hexagons and obtain a smaller nanojoin with the same parameters until one of the special faces contains a heptagon in the boundary. □

For our next proof we need the following technical, but easy lemma:

**Lemma 6.12** *Consider a patch $P$ with two disjoint special faces $S_1$, $S_2$ with $S_2$ being a special t-face. Assume that there are $p$ pentagons and $s$ heptagons in $P$ and let $t = t(S_1)$ and $d = d(S_1)$. Then $s - p = t - d$.*

*Proof* Let $h$ be the number of hexagons in the patch $P$, $t' = t(S_2)$ and $d' = d(S_2)$.

Let $\bar{P}$ be the planar graph obtained by inserting a new vertex into the center of $S_2$ and connecting it to all vertices of degree 2 in $S_2$.

The number of faces $|F|$, edges $|E|$ and vertices $|V|$ of $\bar{P}$ are given by the formulas

$$\begin{aligned} |F| &= p + h + s + t' + 1, \\ 2|E| &= 5p + 6h + 7s + t + d + 3t' + d' \text{ and} \\ 3|V| &= 2|E| + t - (t' - 3). \end{aligned}$$

Using Euler's Formula and the fact that $t' = d'$ we obtain $s - p = t - d$. □

**Definition 8** Let $N$ be a symmetric 5–7 nanojoin with the heptagon at the boundary of the special face $S$. Let $v$ be a vertex of degree 3 in the boundary of $S$ and the heptagon. A maximal path starting at the edge of $v$ that is not contained in $S$, going alternately left and right, with the first turn such that the second edge is contained in the heptagon and containing at most 2 vertices in special faces, is called a 7-cutpath.

**Lemma 6.13** *Let $N$ be a symmetric* 5–7 *nanojoin with the heptagon at the boundary of special face $S$. A* 7*-cutpath $p$ starting in one special face ends in the other.*

*Proof* As the path $p$ is maximal, there are two possibilities: either the last vertex is in the boundary of a special face (so a longer path would contain 3 such vertices), or the next edge following the alternating pattern would intersect the path.

We will show that only the first possibility can occur and that the last vertex is in a different special face to the first one.

Assume first that adding another edge to $p$ would result in revisiting vertex $u$ of $p$, and so would create a cycle $C$. Then $C$ splits $N$ into two components (each containing $C$).

If one of the components, $P$, of $N$ does not contain a special face of $N$, Lemma 3.2 implies $t(P) - d(P) \geq 5$. However, except for $u$, the degrees of the vertices of the boundary of $P$ alternate between 2 and 3, and hence $t(P) - d(P) \leq 2$.

If each component of $N$ contains one special face of $N$, we can apply Lemma 6.12. It implies that the component containing the heptagon has at most as many vertices with degree 3 in the boundary as with degree 2 (and that only if it also contains the pentagon). On the other hand, the degree of $u$ is 3 in this component and the degrees of the other vertices alternate between 2 and 3, with at least one vertex of degree 3 neighbouring $u$ (the one following $u$ in the 7-cutpath). So there are more vertices with degree 3 than with degree 2—a contradiction.

Finally, assume that the 7-cutpath $p$ has both ends in $S$. Note that the second vertex of $p$ can't be in $S$, for if it were then the path would contain only 1 edge and so could not contain two edges of the heptagon. So $p$ splits $N$ into two components and one of them, say $Q$, does not contain a special face of $N$. Both end vertices of $p$ have degree 2 in $Q$, and so contribute 2 to $t(Q) - d(Q)$. The other vertices of $p$ contribute between $-1$ and 1 to $t(Q) - d(Q)$ and the remaining vertices of the special face of $Q$ contribute between 0 and 2. Hence $t(Q) - d(Q) \leq 5$. Together with Lemma 3.2, this implies that $Q$ cannot contain the heptagon. However, knowing that $Q$ does not contain the heptagon implies that $p$ starts with a vertex of degree 3 and that the internal vertices of $p$ contribute 0 or $-1$ to $t(Q) - d(Q)$. So $t(Q) - d(Q) \leq 4$. This contradicts Lemma 3.2.

So the 7-cutpath ends in the other special face. □

In order to prove the next lemma, we will first show how the relative position of endpoints of a path in the boundaries of special faces can be changed. Figure 5 shows how hexagons can be added so that the resulting join has the same parameters, but the endpoint is closer to the concave edge.

When one end of the path is a vertex of a concave edge, the nanojoin and the path can be extended so that the endpoint of the path switches from the $m$-part to the $l$-part of a special face or vice versa. Again, the parameters of the special face do not change. When switching from the $l$-part to the $m$-part a left turn is added, when changing from the $m$-part to the $l$-part a right turn is added. This is depicted in Fig. 6.

**Lemma 6.14** *If there is a symmetric* 5–7 *nanojoin for parameters* $(l, m)$*, there is also a symmetric* 5–7 *nanojoin for parameters* $(l, m)$ *with a legal cutpath.*

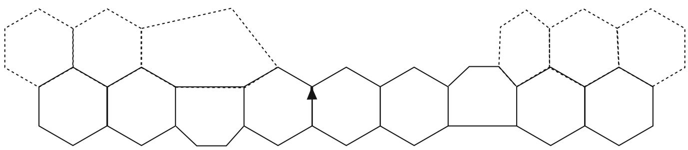


**Fig. 5** Adding hexagons to a special face so that the resulting nanojoin has the same parameters and the path reaches the boundary closer to the concave edge

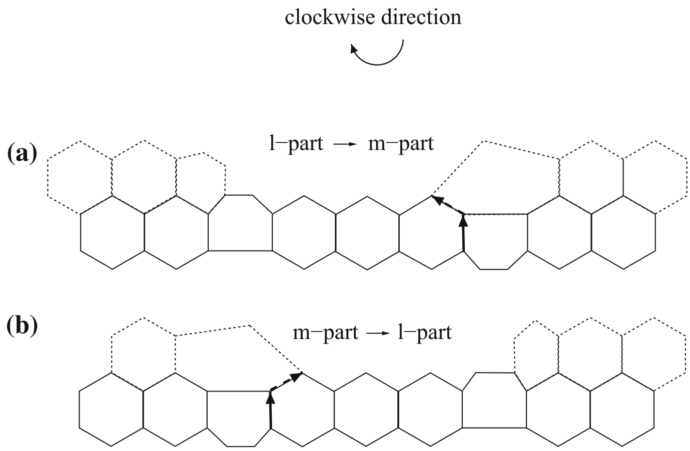
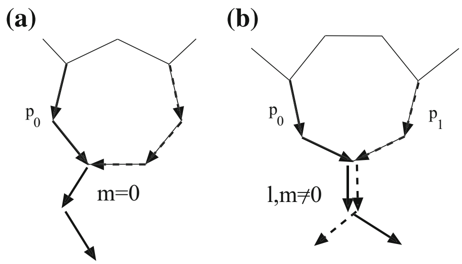



**Fig. 6** Switching one end of a path from the $l$-part to the $m$-part and the other way around

**Fig. 7** The path $p_0$ starting at the heptagon ($m = 0$) and the two paths $p_0$, $p_1$ starting at the heptagon ($m \neq 0$)




*Proof* We will construct a legal cutpath, that is, a path having properties (i), (ii) and (iii) from Definition 4. It will be obvious from the path we start with (alternating left and right) and the operations applied that the resulting path and all intermediate paths have property (iii).

With $r(p)$, respectively $l(p)$ we denote the number of right, respectively left turns of a path $p$ as we traverse $p$ from a chosen start point to a chosen end point.

If there is a symmetric 5–7 nanojoin, due to Lemmas 6.11 and 6.13 there is also one with a heptagon in the boundary and if $m \neq 0$, at the convex edge. There are 7-cutpaths $p_0$ and $p_1$ starting at this heptagon. Interpreting these paths as starting at the heptagon, we choose the indices so that for $p_0$ the first turn of is to the left therefore $r(p_0) + 1 \geq l(p_0) \geq r(p_0)$ and $l(p_1) + 1 \geq r(p_1) \geq l(p_1)$.

When $m = 0$ the path $p_0$ is already a legal cutpath if $r(p_0) = l(p_0)$. If $r(p_0) = l(p_0) - 1$, we can modify the path as shown in Fig. 7a and obtain a path with one more right turn, so that the modified path is a legal cutpath.

So assume now that $m \neq 0$.

If $r(p_0) = l(p_0)$ or $r(p_1) = l(p_1)$, we have found our legal cutpath, possibly after exchanging the two first edges of $p_0$ and $p_1$, which doesn't change the number of left and right turns, but which does change the part in which the path starts.

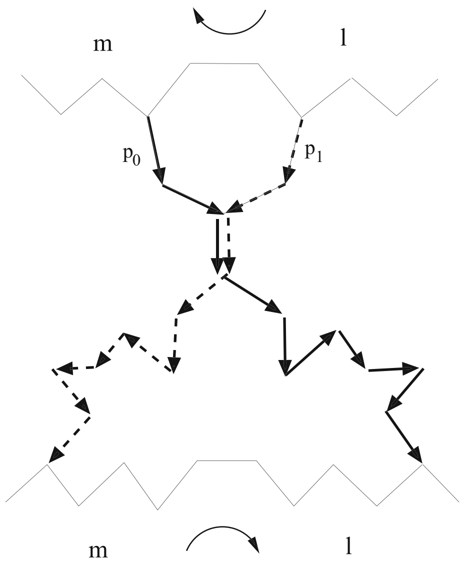



**Fig. 8** The case where neither $p_0$ nor $p_1$ can be made a legal cutpath

So assume $r(p_0) = l(p_0) - 1$ and $r(p_1) - 1 = l(p_1)$. If $p_0$ ends in the $m$-part of the other boundary, we can extend the nanojoin and the path at the other end by repeatedly applying the construction shown in Fig. 5 and then applying the construction of Fig. 6. The path then ends in the $l$-part and has one more right turn. Exchanging the first two edges with $p_1$ we get a legal cutpath. Analogously, we can construct a legal cutpath in the case where $p_1$ ends in the $l$-part.

The last case is that $p_0$ ends after a last left turn in the $l$-part of the other boundary and $p_1$ ends after a last right turn in the $m$-part of the other boundary. Note that there can be no second intersection of $p_0$ and $p_1$ as the segments connecting the two intersections would determine a patch $G$ in the interior with $3 \leq t(G) - d(G) \leq 4$. Depending on whether the other special face is part of $G$, this contradicts Lemmas 3.2 or 6.12.

This situation is, up to additional pairs of right and left turns in the paths or the second special face, depicted in Fig. 8. Together with a segment of the other special face, the parts of the path after the intersection would bound a patch $P$ with $t(P) - d(P) = 3$, which is not possible with at most 1 pentagon and all the rest hexagons (Lemma 3.2). So this last situation is not possible and there is always a legal cutpath. □

Lemma 6.14 together with Theorem 6.4 now gives

**Theorem 6.15** *There is no symmetric* 5–7 *nanojoin.*

We did not discuss equivalence or isomorphism of nanojoins in this article, but as adding one or more hexagons to a nanojoin does not produce a structurally new join, it is natural to define two joins as isomorphic if the infinite graphs obtained by gluing halftubes to the special faces are isomorphic as embedded graphs. With this definition the proofs of Lemma 4.3 and Theorem 5.1 can be slightly modified to show that there are infinitely many nonisomorphic nanojoins with the given properties. For the proof of Lemma 4.2 this is not the case and we conjecture that for 1 pentagon and 1 heptagon the nanojoins are unique:

**Conjecture 6.16** *If* $(a, b) \neq (c, d)$ *and* $a + b \geq 2,\ c + d \geq 2$*, there is up to isomorphism exactly one nanojoin with* $p = s = 1$ *joining two halftubes with parameters* $(a, b)$ *and* $(c, d)$.

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