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Identification of and symmetry computation for crystal nets

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Exact methods are presented to determine whether two periodic nets are combinatorially isomorphic and to compute the full combinatorial symmetry group of a net. It is found that for a large class of nets, which includes all known zeolite nets and most other known crystal nets, this group can be realized as a crystallographic space group.

1. Introduction

Three-dimensional nets play an important role in the qualitative analysis and description of crystal structures. In the simplest case, the net associated with a crystal consists of vertices representing individual atoms and connecting edges representing bonds. In other applications, vertices may represent clusters of atoms and edges may represent more or less complicated linkers (*e.g.* Yaghi *et al.*, 2003).

A net is usually considered as a graph with some special properties, but there seems to be no generally accepted precise definition. For our purposes, a net will always be a connected three-periodic graph as defined in the next section.

Some nets underlie a great variety of crystal species of different compositions. An important example is the diamond net, which appears, for example, in elemental carbon and in the cristobalite form of SiO_2 (with Si atoms as vertices and —O— links as edges). Considerable effort has been devoted to the enumeration of nets (*e.g.* Barrer & Villiger, 1969; Wells, 1977, 1979; Chung *et al.*, 1984; Smith, 1988; Akporiaye & Price, 1989; O'Keeffe, 1991, 1992, 1995; O'Keeffe & Brese, 1992; Beukemann & Klee, 1992; Han & Smith, 1994, 1999*a*,*b*; Andries & Smith, 1994; Bader *et al.*, 1997; Treacy *et al.*, 1997; Delgado-Friedrichs *et al.*, 1999; Delgado-Friedrichs & Huson, 2000). The *Database of Zeolite Framework Types* (Baerlocher *et al.*, 2001), currently comprising 139 entries, lists all nets that appear as frameworks of actual zeolitic materials. Many nets can be realized as embeddings in which edges are all of equal length and correspond to shortest intervertex distances. Such structures are called sphere packings and systematic enumerations of many of them have been given (Fischer, 1973, 1974, 1991*a*,*b*, 1993; Koch & Fischer, 1995; Fischer & Koch, 2002). In order to describe a structure qualitatively, a reliable method to identify the underlying net is essential. Invariants like coordination sequences (Fischer, 1973; Brunner, 1979), eigenvalue spectra (Klee, 1987) or vertex symbols (Fischer, 1973; O'Keeffe & Brese, 1992) are frequently used to look up entries in such listings. It is well known, however, that none of these are completely reliable to identify nets.

Often crystal nets are considerably distorted from their maximal or *idealized* symmetry group. It seems that up to now there has been no systematic way to determine either the combinatorial or the maximal embeddable symmetry group of a net. Consequently, structures are quite frequently reported with the wrong symmetry. In actual or predicted crystal structures with a given embedding, a number of methods have been developed to determine the correct symmetry group (LePage, 1987; Hester & Hall, 1996; Hannemann *et al.*, 1998); it is useful in this context to know the maximal embeddable symmetry group that serves as an upper bound.

In this paper, we present an informal account of a systematic mathematical approach to both problems. Its key ingredients are the so-called *vector representation* of periodic graphs as proposed by Chung *et al.* (1984), the method of *equilibrium*, or *barycentric placement*, inspired by Tutte (1960, 1963), and exact arithmetic using rational numbers of arbitrary precision. A detailed treatment of the mathematical aspects including complete proofs can be found in Delgado-Friedrichs (2003). In the following, we take the freedom to skip certain technicalities, concentrating on the underlying ideas.

2. Representing nets

For our purposes, a *graph* consists of a set of *vertices* and a set of *edges*, each connecting two vertices. If v and w are vertices connected by an edge, they are called *neighbors* and the connecting edge is written (v, w) or (w, v). There may be at most one edge between any given pair of vertices. No vertex may be its own neighbor. No vertex may have infinitely many neighbors.

The vertices themselves are essentially just labels. The interesting structural properties of a graph lie in the arrangement of edges. Thus, an *isomorphism* between graphs is a *bijective* (one-to-one and onto) function f that maps vertices of the first onto vertices of the second, where $f(v)$ and $f(w)$ are neighbors if and only if v and w are neighbors. The edge connecting $f(v)$ and $f(w)$ is written $f(v, w)$. Two graphs are *isomorphic*, that is, essentially or structurally equal, if there

is an isomorphism between them. A (combinatorial) *symmetry* is a self-isomorphism of a graph.

A *3-periodic graph* is an infinite graph with an abstract $P1$ symmetry. This means that, at first, we do not assign coordinates to vertices, but still allow formal translates, so, for example, if v is a vertex, $v + (1, 0, 0)$ is its image translated by one unit along the x axis. This makes sense if we interpret v as a triplet (v_x, v_y, v_z) of variables, thus $v + (1, 0, 0) = (v_x + 1, v_y, v_z)$. Once we assign actual coordinates to v, all its translates obtain coordinates as well. We allow only finitely many types of non-equivalent vertices (*i.e.* not related by translations). The set of translates of v is given by all expressions of the form $v + \mathbf{s}$, where $\mathbf{s}$ is a three-dimensional integer vector.

Crystal nets are obvious examples of periodic graphs. In the following, a *net* will always be a connected 3-periodic graph.

Isomorphisms of periodic graphs are required to respect the periodicity. This means that, if f is an isomorphism and $\mathbf{s}$ is an integer vector, there is another integer vector $\mathbf{s}'$ such that, for every vertex v, we have $f(v + \mathbf{s}) = f(v) + \mathbf{s}'$. We consider $\mathbf{s}'$ the image of $\mathbf{s}$ under some function f^*, which maps integer vectors to integer vectors. Because $f(v) + f^*(\mathbf{s} + \mathbf{t}) = f(v + \mathbf{s} + \mathbf{t}) = f(v + \mathbf{s}) + f^*(\mathbf{t}) = f(v) + f^*(\mathbf{s}) + f^*(\mathbf{t})$ for every vertex v and every pair of integer vectors $\mathbf{s}$ and $\mathbf{t}$, f^* must be linear. Because f is an isomorphism, it must map the translates of v bijectively onto the translates of $f(v)$. This implies that f^* is bijective. Put yet another way, the matrix describing f^* has only integer entries and its determinant is either 1 or -1. Such matrices are called *unimodular*. Self-isomorphisms of periodic graphs are also called periodic symmetries in the following.

There is a natural way to encode a periodic graph, which Chung *et al.* (1984) have called the *vector method* and proposed as a basis for representing and enumerating nets. This is implemented as follows.

Take a representative for each type of vertex up to translation. Call these $v_1, \ldots, v_n$, where n is the number of types. Now each vertex of the net can be uniquely written in the form $v_i + \mathbf{s}$ for an appropriate integer i and an appropriate vector $\mathbf{s}$. An edge e can be written in two ways, one with each of its vertices first. We obtain a unique form $e = (v_i + \mathbf{s}, v_j + \mathbf{t})$ once we require that either i is smaller than j or else i and j are equal and $\mathbf{s}$ is lexicographically smaller than $\mathbf{t}$.

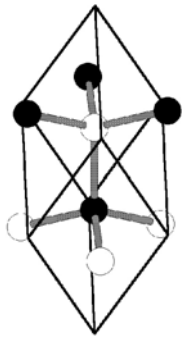

Figure 1
A primitive unit cell of the diamond structure. Open circles = atom 1 and translates. Filled circles = atom 2 and translates.

Clearly, the edge e above has a translate $[v_i, v_j + (\mathbf{t} - \mathbf{s})]$. In order to describe a net completely therefore, we only have to list all edges of the form $(v_i, v_j + \mathbf{s})$, where either $i < j$ or else $i = j$ and the first non-zero coordinate of $\mathbf{s}$ is positive. As an example, the 6-coordinated net corresponding to the primitive cubic lattice can be represented as

```
1 1   1 0 0
1 1   0 1 0
1 1   0 0 1,
```

where a line of the form *ij xyz* represents the edge $[v_i, v_j + (x, y, z)]$.

The diamond net (Fig. 1) can be written

```
1 2   0 0 0
1 2   1 0 0
1 2   0 1 0
1 2   0 0 1.
```

Obviously, the encoding for a net depends on the choice of vertex representatives. As an example, if we exchange the roles of v_1 and v_2 in the diamond net, we obtain the representation

```
1 2    0   0   0
1 2   −1   0   0
1 2    0  −1   0
1 2    0   0  −1.
```

Furthermore, a unimodular transformation applied to all vector components of a representation results in a representation of an isomorphic graph. Thus, the net represented by

```
1 1   1 1 1
1 1   0 1 1
1 1   0 0 1
```

is isomorphic to the primitive cubic net, because the transformation given by the matrix

$$\begin{pmatrix} 1 & 1 & 1 \\ 0 & 1 & 1 \\ 0 & 0 & 1 \end{pmatrix}$$

is unimodular.

In order to identify isomorphic nets easily, one would like to have some canonical representation, *i.e.* an encoding that only depends on the isomorphism type of a net, not on the way it was originally specified. A simple idea to achieve this is to read all possible representations for a given net as linear strings of integers and choose the lexicographically smallest of these. To obtain a unique string for each representation, we sort the lines lexicographically before forming the string. For example, the two encodings for the diamond net seen so far correspond to the strings

```
120001200112010121 00
```

and

```
12–100120–101200–112000,
```

the second of which is smaller (it has a -1 at the third position).

Whenever there is more than one type of vertex up to translation, we can choose the representative for the second type arbitrarily far from the first, which leads to infinitely many different representations of the same graph. For instance, if a, b, c is an arbitrary triplet of integers, we can write the diamond net as

$$\begin{array}{lllll} 1 & 2 & a & b & c \\ 1 & 2 & a+1 & b & c \\ 1 & 2 & a & b+1 & c \\ 1 & 2 & a & b & c+1, \end{array}$$

where the second representative is chosen to be the translate by $(-a, -b, -c)$ of the one used originally. To avoid this, we postulate the following first requirement for a 'good' representation, *i.e.* one that can be used in the search for a canonical one: in a good representation, the set of representatives $v_1, \ldots, v_n$ for the types of vertex should always be *connected* in the sense that the finite graph consisting of the representatives and all the edges connecting these is a connected graph.

There are also infinitely many unimodular matrices, again leading to potentially infinitely many distinct representations of the same graph. Indeed, every matrix

$$\begin{pmatrix} 1 & a & b \\ 0 & 1 & c \\ 0 & 0 & 1 \end{pmatrix}$$

is unimodular. This can be resolved by requiring that, in a good representation, each of the three 'standard' base vectors (1, 0, 0), (0, 1, 0) and (0, 0, 1) must appear.

In virtually all crystal nets, both requirements for good representations can be fulfilled and together imply that the collection of good representations for any net is finite. So, in principle, one could write a computer program to generate all good representations of a given net and pick the smallest. Because the set of good representations does not depend on the way the net was originally specified, the chosen representation would be truly unique and represent an isomorphism type of net unambiguously. Unfortunately, the number of good representations grows rapidly with the number of types of vertex. Moreover, it is hard to come up with efficient generation methods that do not produce the same representation over and over again.

In order to determine isomorphisms and symmetries of nets effectively with a computer, we need more restrictive requirements for the set of good representations and fast algorithms to compute all of them.

The methods described below can be shown to be *computationally efficient* in the sense that the number of steps required for a net with m edges in the unit cell is proportional at most to a polynomial in m. They have been implemented in the computer program *Systre* and been successfully applied to nets with up to several hundreds of vertices in the unit cell, among them all the zeolite framework types (Baerlocher *et al.*, 2001).

3. Equilibrium placement

In a net derived from an actual crystal, atom positions can be used to find some of the symmetries. The problem here is that the net may not be in a configuration of highest symmetry and, even if so, such a configuration is not unique in any but the most regular nets, as for example diamond. Accordingly, it is better to disregard the coordinates and concentrate on the pure topology of the net. As we have seen above, however, such an approach leads to a whole new range of problems. Why can we not find the perfect configuration for any given net, one that has all the possible symmetries and does only depend on the topology?

As it turns out, we can, or almost so. Although we find it convenient to describe this perfect placement in terms of forces, energy and equilibria, one must bear in mind that these do not constitute any reasonable physical model. Indeed, our model only works in the abstract domain of infinite periodic graphs. It is, however, an extremely useful tool, as the program *Systre*, already mentioned above, demonstrates.

Let us say a *placement* is a function p that assigns coordinates to the vertices of a graph. For a periodic graph, we require placements to be periodic, *i.e.* to satisfy $p(v + \mathbf{s}) = p(v) + p^*(\mathbf{s})$, where p^* is some linear transformation. We say that a placement is in *equilibrium* if every vertex is placed in the center of gravity of its neighbors (barycentric coordinates), *i.e.* if

$$p(v) = \frac{1}{|N_v|} \sum_{w \in N_v} p(w), \qquad (1)$$

where N_v is the set of neighbors and $|N_v|$ is the number of neighbors, or *degree*,[1] of v. The treatment was inspired by Tutte (1960, 1963) and uses ideas going back to Maxwell (1864, 1870). Imagine an attractive force between each pair of connected vertices proportional to their distance. Because (1) is equivalent to

$$0 = \frac{1}{|N_v|} \sum_{w \in N_v} p(w) - p(v),$$

equilibrium placements are precisely those for which all forces are balanced.

For a finite graph, this can only happen if all vertices are placed at the same point. The reason is simply that otherwise there must be vertices that are maxima or minima in some directions, preventing them from being in equilibrium. For nets, however, this is no longer true. Indeed, it has been shown (Delgado-Friedrichs, 2003) that every connected periodic graph, *i.e.* every net, has a periodic equilibrium placement, which is essentially unique.

Obviously, (1) still holds after applying a translation or linear transformation to all coordinates. Consequently, we may set p^* to the identity and assume all positions are expressed in dimensionless crystallographic coordinates. We

[1] The degree of a vertex is often called its connectivity by chemists (*e.g.* Wells, 1977). We avoid that term because the connectivity of a graph has a completely different meaning in graph theory. Thus, for a net in which all vertices are of degree 4, we prefer '4-coordinated net' instead of '4-connected net'.

may also assume that one vertex, say v_1, is placed at the origin and all its translates similarly fixed. The solution of the equilibrium equation is then independent of a particular metric tensor or origin choice.

It is easy to see that a periodic equilibrium placement corresponds to a critical point (derivative equal to zero) of the 'energy' function defined as

$$E_p = \sum_{(v,w)} d(p(v), p(w))^2, \qquad (2)$$

where d is the distance and the summation is over the types of edge up to translation. Under the condition mentioned above that v_1 is placed at the origin, one can show (Delgado-Friedrichs, 2003) that, for every net and every choice of metric tensor, the energy function has exactly one critical point.

Because this theorem is crucial for all the following, we sketch the proof: first assume that all the vertex representatives are placed at the same point, which we may safely assume to be the origin. In this configuration, the energy function (2) attains some positive value E_0. For any other placement p, consider

$$D_p = |p(v_1)|^2 + \ldots + |p(v_n)|^2$$

the sum of squares of displacements of the vertex representatives from the origin. We argue that, for any $E > E_0$, there is some D such that, whenever $D_p > D$, we have $E_p > E$. The reason is simply that, because nets are assumed to be connected, a large enough value of D_p means that there must be at least one very long edge, long enough to make E_p as large as necessary. This in turn means that E_p, which is a quadratic function by definition, is nondegenerate, and therefore has a unique critical point, in this case a minimum (*cf.* Richter-Gebert, 1996, ch. 12).

It is interesting to note that, although the value of E_p depends on a particular metric, the equilibrium placement itself does not. We do, however, obtain different solutions for different representations of the same graph. Recall that a particular representation depends on a choice and ordering of vertex representatives and a choice of lattice basis and origin. Consequently, the lists of equilibrium coordinates for the vertex representatives in different representations may differ by a permutation of points, a global (unimodular) change of basis and origin plus integral shifts of individual points. For any given representation, an equilibrium placement can be determined by solving the system of linear equations derived from (1), taking into account the fact that some neighbors may be translates of vertex representatives. An example will be given in the following section. The resulting coordinates are all rational numbers, so they can be computed precisely using arbitrary length rational instead of floating-point arithmetic.

We call a net *stable* if in equilibrium no two vertices are at the same place. This means that, in stable nets, each vertex can be identified by its equilibrium position, a fact that will be useful later. There are, up to translation, only finitely many periodic symmetries of a given net. These correspond, after choosing a suitable metric, to a finite list of isometries of its equilibrium placement, which, together with the translations, form a crystallographic group. To see this, recall that the effect of applying a periodic symmetry f to some vertex v and its translates is expressed by mapping v to some, possibly inequivalent, vertex w and applying a unimodular matrix, say **M**, to each translation vector.

Consider the following pair of new placements: For the first, associate with each vertex the position of its f image in the original placement. For the second, apply the matrix **M** to the list of original positions, then translate the result until v is placed at the same position as w was in the original placement. A transformation that can be expressed as applying a matrix followed by a translation is generally called affine. It is immediate that the affine image of an equilibrium placement is still an equilibrium placement. In effect, the two new placements are both in equilibrium and assign, by construction, the same coordinates to v and each of its translates. As seen above, they must then be identical, so the effect of applying a periodic symmetry to the positions in an equilibrium placement can be expressed as an affine transformation.

Because the resulting list of affine symmetries up to translation is finite, by a standard argument we can find a metric that turns them all into isometries.

One should note, however, that the correspondence is not always one-to-one. For certain, necessarily non-stable, nets there are non-trivial periodic symmetries that are associated with the identity transformation. An example appears in §6 (Fig. 3). However, for stable nets we use the theorem (Delgado-Friedrichs, 2003) that the group of combinatorial periodic symmetries of a stable net is isomorphic to the maximal crystallographic symmetry group that can be achieved by a placement for that net.

4. Computing with equilibrium placements

We now use an extended example to further illustrate the vector method as well as equilibrium placements and show how to employ these in computations. We use the Si net (Fig. 2) of the moganite form of SiO_2 (Miehe & Graetsch, 1992) with symmetry group $I2/a$ as our example (the edges of the net correspond to —O— links between Si atoms at the vertices of the net) as it is a good example of a net of higher combinatorial symmetry group, *Cmmm* (*cf.* O'Keeffe & Hyde, 1996).

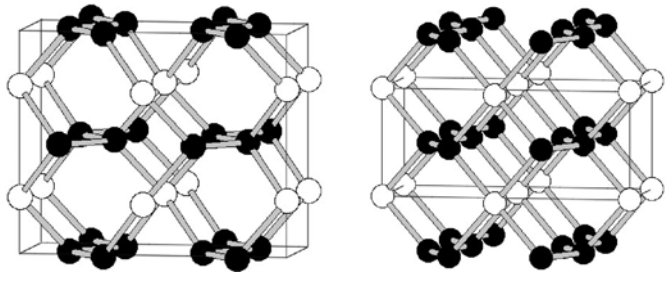

Figure 2
The moganite net as originally input to *Systre* (left) with symmetry $I2/a$ (**a** vertical and **c** horizontal on the page) and as output with a smaller cell (right) with symmetry *Cmmm* (**c** vertical).

From a primitive cell of the crystal (any unit cell will do), which contains six Si atoms, we derive the following net representation from a knowledge of the atoms' neighbors:

$$\begin{array}{ccrrr} 1 & 3 & 0 & 1 & 1 \\ 1 & 4 & 0 & 0 & 0 \\ 1 & 5 & -1 & 0 & 0 \\ 1 & 6 & 1 & 0 & 0 \\ 2 & 3 & 1 & 0 & 0 \\ 2 & 4 & -1 & 0 & 0 \\ 2 & 5 & 0 & -1 & -1 \\ 2 & 6 & 0 & 0 & 0 \\ 3 & 4 & -1 & -1 & 0 \\ 3 & 4 & -1 & 0 & 0 \\ 5 & 6 & 1 & 0 & 0 \\ 5 & 6 & 1 & 1 & 0. \end{array} \tag{3}$$

This is the *only* information about the net that we subsequently use.

Denote the equilibrium coordinates of vertices 1 up to 6 by (x_1, y_1, z_1) up to (x_6, y_6, z_6). From (1), the equilibrium conditions for the x coordinates are

$$\begin{aligned} 4x_1 &= (x_3 + 0) + (x_4 + 0) + (x_5 - 1) + (x_6 + 1) \\ 4x_2 &= (x_3 + 1) + (x_4 - 1) + (x_5 + 0) + (x_6 + 0) \\ 4x_3 &= (x_1 - 0) + (x_2 - 1) + (x_4 - 1) + (x_4 - 1) \\ 4x_4 &= (x_1 - 0) + (x_2 + 1) + (x_3 + 1) + (x_3 + 1) \\ 4x_5 &= (x_1 + 1) + (x_2 - 0) + (x_6 + 1) + (x_6 + 1) \\ 4x_6 &= (x_1 - 1) + (x_2 - 0) + (x_5 - 1) + (x_5 - 1), \end{aligned} \tag{4}$$

which is readily simplified, yielding

$$\begin{aligned} x_2 &= x_1 \\ x_3 &= x_1 - \tfrac{1}{2} \\ x_4 &= x_1 + \tfrac{1}{2} \\ x_5 &= x_1 + \tfrac{1}{2} \\ x_6 &= x_1 - \tfrac{1}{2}. \end{aligned} \tag{5}$$

To understand how (4) is derived from (1) and (3), consider the third line of (4), which is the result of applying (1) to the x coordinate of the third vertex representative v_3. There are four lines in (3) that refer to v_3, namely

$$\begin{array}{ccrrr} 1 & 3 & 0 & 1 & 1 \\ 2 & 3 & 1 & 0 & 0 \\ 3 & 4 & -1 & -1 & 0 \\ 3 & 4 & -1 & 0 & 0. \end{array}$$

Flipping the first two lines to move the 3 to the front and negating the shift vectors in those rows accordingly yields

$$\begin{array}{ccrrr} 3 & 1 & 0 & -1 & -1 \\ 3 & 2 & -1 & 0 & 0 \\ 3 & 4 & -1 & -1 & 0 \\ 3 & 4 & -1 & 0 & 0. \end{array}$$

Thus, the neighbors of v_3 are $v_1 + (0, -1, -1)$, $v_2 + (-1, 0, 0)$, $v_4 + (-1, -1, 0)$ and $v_4 + (-1, 0, 0)$, the first coordinates of which are just $(x_1 - 0)$, $(x_2 - 1)$, $(x_4 - 1)$ and $(x_4 - 1)$.

Setting $x_1 = 0$ and applying (5) yields $x_2 = 0$, $x_3 = x_6 = -1/2$ and $x_4 = x_5 = 1/2$. The complete set of equilibrium coordinates with $v_1 = (0, 0, 0)$ is

$$\begin{aligned} v_1 &= (0, 0, 0) \\ v_2 &= (0, -\tfrac{1}{2}, -\tfrac{1}{2}) \\ v_3 &= (-\tfrac{1}{2}, -\tfrac{3}{4}, -\tfrac{7}{12}) \\ v_4 &= (\tfrac{1}{2}, -\tfrac{1}{4}, -\tfrac{5}{12}) \\ v_5 &= (\tfrac{1}{2}, \tfrac{1}{4}, \tfrac{1}{12}) \\ v_6 &= (-\tfrac{1}{2}, -\tfrac{1}{4}, -\tfrac{1}{12}). \end{aligned} \tag{6}$$

Note that a fraction like $1/12$ cannot be represented exactly by a decimal or binary number. It is essential, however, to do all subsequent calculations with its precise value. Remember that we are not dealing with physical models, and equilibrium positions of distinct vertices may be arbitrarily close without being identical. Consequently, all calculations are with fractions and, in computer implementations, rational arithmetic with arbitrarily long numerators and denominators has to be used.

It is useful to represent nets in terms of a smallest possible unit cell in all calculations. A real crystal structure, however, may well be distorted beyond recognition from its ideal primitive setting. Our first task therefore is to find additional combinatorial translations, which, by the previous section, must occur as actual translations of the equilibrium form. If there is one in our example net, it must shift v_1 to one of the other representatives. Assume first that v_1 is shifted to v_3. Then v_3 is shifted to some other vertex that has z coordinate $2z_3 = -14/12$. But this z coordinate does not occur in any vertex of the net because none of the representatives has one that can be derived from $-14/12$ by adding or subtracting an integer. We conclude that v_3 cannot be a translate of v_1, and by a similar argument exclude v_4, v_5 and v_6 as well.

It remains to inspect the shift by $(0, -1/2, -1/2)$, which maps v_1 to v_2. Clearly, it shifts each vertex to some other vertex, namely

$$\begin{aligned} v_1 &\to v_2 \\ v_2 &\to v_1 - (0, 1, 1) \\ v_3 &\to v_6 - (0, 1, 1) \\ v_4 &\to v_5 - (0, 1, 1) \\ v_5 &\to v_4 \\ v_6 &\to v_3. \end{aligned}$$

We have to check whether this mapping of vertices induces a mapping of edges. For example, the edge $(v_1, v_3 + (0, 1, 1))$ represented by the first line in (3) is shifted to $(v_2, (v_6 - (0, 1, 1)) + (0, 1, 1)) = (v_2, v_6)$, which, by line 8 in (3), is an edge, while the edge $(v_3, v_4 + (-1, 0, 0))$ from line 10 maps to $(v_6 - (0, 1, 1), (v_5 - (0, 1, 1)) + (-1, 0, 0))$, which by flipping and shifting accordingly can be seen to be in the same class as $(v_5, v_6 + (1, 0, 0))$, or line 11. When all tests are done, it turns out that we have indeed found a new symmetry, and that (3) can be replaced by a smaller representation of the same net. To obtain it, we choose a new set of vertex representa-

tives, *e.g.* $w_1 = v_2$, $w_2 = v_3$ and $w_3 = v_4$, and a basis for the translation lattice generated by the old unit translations and the newly found translation $(0, -1/2, -1/2)$. We use $(1, 0, 0)$, $(0, 1, 0)$ and $(0, 1/2, 1/2)$ as base vectors. Then $v_1 = w_1 + (0, 0, 1)$, $v_5 = w_3 + (0, 0, 1)$ and $v_6 = w_2 + (0, 0, 1)$ in terms of the new basis in which $(0, 0, 1)$ is $(0, 1/2, 1/2)$ in the old basis. Mapping all edges from (3) accordingly, sorting and removing duplicates, we obtain:

$$\begin{array}{rrrrr} 1 & 2 & 1 & 0 & 0 \\ 1 & 2 & 0 & 0 & 1 \\ 1 & 3 & -1 & 0 & 0 \\ 1 & 3 & 0 & 0 & -1 \\ 2 & 3 & -1 & -1 & 0 \\ 2 & 3 & -1 & 0 & 0. \end{array} \tag{7}$$

For example, $(v_2, v_5 + (0, -1, -1))$ from line 7 of (3) becomes $(w_1, (w_3 + (0, 0, 1)) + (0, 0, -2)) = (w_1, w_3 + (0, 0, -1))$, because the vector $(0, -1, -1)$ in the old basis clearly becomes $(0, 0, -2)$ in the new one.

The new representation must be minimal because all potential additional translations have already been excluded in the old one. The new equilibrium coordinates are

$$\begin{aligned} w_1 &= (0, 0, 0) \\ w_2 &= (-\tfrac{1}{2}, -\tfrac{1}{6}, -\tfrac{1}{6}) \\ w_3 &= (\tfrac{1}{2}, \tfrac{1}{6}, \tfrac{1}{6}). \end{aligned} \tag{8}$$

These can be computed either from scratch or from the equilibrium coordinates for the old representation.

Our next task is to determine all the combinatorial symmetries of our net and by these to recognize its ideal space group. A general strategy for this is as follows: each symmetry maps edges to edges. If we find a triplet of directed net edges in linearly independent directions, *i.e.* such that their associated vectors do not lie in a common plane, the images of these by some symmetry completely determine an affine mapping. More precisely, we use only the starting point of the first and the directions of all three edges, which means that it does not matter if we replace some edge by a translate. Every mapping that can be constructed in this way has to be tested to see if it maps all edges to edges (and, consequently, all vertices to vertices). There are only finitely many types of edge up to translation and thus only finitely many affine maps to check.

In practice, it is usually sufficient to test a considerably smaller number of potential symmetries. Let us take a look at the vertices and their neighborhoods. Vertex w_1 at $(0, 0, 0)$ has its four neighbors at $(1/2, -1/6, -1/6)$, $(-1/2, -1/6, 5/6)$, $(-1/2, 1/6, 1/6)$ and $(1/2, 1/6, -5/6)$. These four points clearly lie on a common plane. This is not the case for the neighbors of w_2 or w_3. An affine symmetry must preserve coplanarity of points and can therefore only map translates of w_2 or w_3 to translates of w_2 or w_3 and translates of w_1 to translates of w_1. Any new symmetry is found among the following eight possible mappings. Indeed, if w_2 is left fixed, all its neighbors stay fixed, or only the w_1-type neighbors are swapped, or only the w_3-type neighbors are swapped, or both pairs of neighbors are. If w_2 is mapped to w_3, there are four analogous possibilities, derived by first applying any of the four mappings that leave w_2 fixed and then mapping w_2 to w_3 with one specific mapping of their neighbors. Consider the first non-trivial choice, namely that w_2 stays fixed and its w_1 neighbors are swapped. This means in particular that the point $(-1, 0, 0)$ is mapped onto $(0, 0, -1)$ and *vice versa*, while $(-1/2, -5/6, 1/6)$ and $(-1/2, 1/6, 1/6)$ stay fixed. This is achieved by the unique affine transformation, which can be written as a multiplication with the matrix

$$\mathbf{A_1} = \begin{pmatrix} -1 & 0 & 2 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

followed by a translation by $\mathbf{t}_1 = (-1, 0, 1)$.[2] To see if this induces a symmetry of the net, it remains to check only those two types of edges that do not involve w_2, namely $(w_1, w_3 + (-1, 0, 0))$ and $(w_1, w_3 + (0, 0, -1))$. Because w_1 is mapped to $(-1, 0, 1)$, which is the position $w_1 + (-1, 0, 1)$ and w_3 is mapped to $w_3 + (-2, 0, 2)$, we see immediately that these two edge types are exchanged with each other and that we have indeed found a symmetry.

In the same way, one checks that keeping w_2 fixed while swapping its w_3 neighbors yields a symmetry, expressed by the affine transformation with matrix

$$\mathbf{A}_2 = \begin{pmatrix} 1 & -1 & 0 \\ 0 & -1 & 0 \\ 0 & -1 & 1 \end{pmatrix}$$

and vector $\mathbf{t}_2 = (0, -1, 0)$. Both symmetries can be combined to yield the fourth possibility of keeping w_2 fixed while swapping both neighbor pairs. Finally, we have to consider symmetries that exchange translates of w_2 with translates of w_3. By the above, either all four potential ways of doing this work or none of them does. As it turns out, w_3 and its neighbors can be derived from w_2 and its neighbors by a simple inversion at the origin. This turns out to be a symmetry of the whole net, as well, with matrix

$$\mathbf{A}_3 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

and vector $\mathbf{t}_3 = (0, 0, 0)$. Consequently, all eight potential ways of defining a symmetry of our net work, and we have found three affine symmetries that, together with the translations, generate the full symmetry group. Note, however, that these may appear in a form very different from the usual crystallographic conventions. Indeed, the original lattice basis and origin may not fit well to the newly found symmetries. *Systre* uses the *sgtbx* package by Grosse-Kunstleve *et al.* (2002), which recognizes the space group and transforms the generators into a conventional form according to *International Tables for Crystallography* (Hahn, 1996). The *sgtbx* package first converts the given list of symmetries to a form obeying crystallographic conventions, then tries to construct a change

[2] Notice that we treat coordinates as row vectors so in this case a new coordinate triple (w') is obtained from the old (w) by $w' = w\mathbf{A}_1 + \mathbf{t}_1$.

of basis matrix for each of the 230 standard settings as tabulated in *International Tables*. Because the results obtained by *Systre* are not always readily processed by *sgtbx*, some of the preprocessing steps are duplicated in a slightly more general form before feeding it the symmetries. In particular, point symmetries are analyzed to compute a preliminary basis, which is then refined according to the present translation lattice, which determines the centering. Finally, a suitable origin is chosen. For our example, the space group turns out to be *Cmmm* (see the illustration in Fig. 2).

5. Canonical forms

In order to represent a periodic graph in the fashion as described in §2, two pieces of information are required. First, an ordered set of vertex representatives and, second, a basis for the translation lattice. Every periodic graph is – up to isomorphism – completely and uniquely determined by the collection of all its representations. Unfortunately, as noted before, there are infinitely many of those, which is why the notion of a *good* representation was introduced. Generating the set of all good representations for a given periodic graph is a finite problem. Because this set is always the same, no matter how the graph was presented originally, we can, by picking the lexicographically smallest of all good representations, be sure to find a canonical form by which the graph can be uniquely identified.

The number of good representations may, however, be huge. For any graph with n types of vertex and any good representation of that graph, we may permute the order in which the numbers 1 up to n are assigned to the vertex representatives in any possible way as to obtain another, potentially different, good representation. In effect, the number of good representations for a graph with n kinds of vertex is at least of the order of $n!$, which makes actual computation unfeasible for all but the very simplest graphs. Our goal must therefore be to find a considerably smaller set of representations, which is still characteristic in the sense that it does not depend on the form in which the graph was originally specified, but only on its isomorphism type.

Assume we are given a periodic graph together with its equilibrium placement and for none of its vertices is there a pair of neighbors that occupy the same position in space in the equilibrium placement. We call such graphs *neighbor-unique* for the moment. Assume also that we have picked an arbitrary vertex, v, and an arbitrary basis, B, of $\mathbf{Q}^3$ (the three-dimensional space of rational numbers), which does not necessarily have to be a basis for the translation lattice. Our claim is that, relative to the pair (v, B), we can construct a unique representation for the original graph, and we only have to consider a small number of pairs (v, B).

This works as follows: first, all coordinates and translation vectors are expressed in terms of the basis B. After that, we build the set of vertex representatives step by step, assigning vertex numbers from 1 up to n. We use two variables t (for tail of queue) and h (for head of queue), where h is the next-lowest vertex number that remains to be assigned, and t is the lowest number of a vertex representative that has not yet been completely processed. At startup, v is assigned vertex number 1, t is set to 1 and h is set to 2. As long as t is less than or equal to n, we consider the set of neighbors of the vertex representative with vertex number t. Because of neighbor uniqueness, each of these has a different position in space, which we consider in terms of the basis B. Neighbors of vertex representative t are then processed in lexicographical order with respect to the resulting coordinate vectors. If a neighbor is a translate of a vertex representative already found, say the one with number s, the corresponding translation (x, y, z), in terms of B, is determined and the edge $(v_t, v_s + (x, y, z))$ is stored. Otherwise, if a neighbor is no such translate, it becomes the next representative and is assigned vertex number h. The edge $(v_t, v_h + (0, 0, 0))$ is stored and h is incremented. Once all neighbors of v_t are processed in this way, t is incremented.

When this process is finished, we obtain a list of edge representatives. These do not necessarily form a representation for the given periodic graph in the sense of §2 because we did not require B to be a basis of the translation lattice. Consequently, it remains to find such a basis. This is fairly easy: take all the translation vectors appearing in the edge list and form a matrix having these as its rows. Then triangulate that matrix using row operations and integer arithmetic. In order to make this process canonical, it is essential that the triangulation is performed in a well defined deterministic way so as to always obtain the same result. Finally, all edge representatives must be converted to the newly found lattice basis. Notice that the graph representation thus obtained is not necessarily good in the sense of §2. This is not a serious problem, however, because the set of vertex representatives is clearly connected and it is fairly easy to obtain a good representation from it, if one exists.

The representation thus constructed is unique given a start vertex v and a rational basis B. Thus, if we can find a relatively small set of pairs (v, B) that is characteristic for a graph up to isomorphism, we are done. But such a set can be obtained in the same way as for the symmetry computation described in §4: consider all possible ordered triplets of directed edge representatives, the direction vectors of which do not lie in a common plane. Take the start vertex of the first edge as v and take the direction vectors of all three to form B. For a graph with m kinds of edge up to translation, there are at most $8m(m-1)(m-2)$ such edge triplets to consider.

The number of triplets can usually be reduced significantly by requiring that as many of the directed edges as possible start from a common vertex. For three-dimensional nets, this means that either all three must start at the same vertex v or, if that is not possible, as, for example, happens in the NbO net (in which all vertices have square-planar coordination), the first two must start at a common vertex. There is always at least one vertex with not all of its neighbors on a common line, because otherwise the net could not be more than one-dimensional. In the simplified example from §4, there are thus two possible starting vertices, w_2 and w_3. For each of those, $4 \times 3 \times 2$ edge triplets have to be considered, giving a total of 48 (v, B) pairs. To further reduce that number, we observe that

edge triplets that are symmetric images of each other will produce identical representations. In our example, this means that we need only consider six out of 48 (v, B) pairs in order to compute a canonical form. Because w_2 and w_3 are related by symmetry, we use $v = w_2$ as the starting vertex in all these. It is convenient to exchange the roles of w_2 and w_1 so as to make further computations easier, thus setting $u_1 = w_2$, $u_2 = w_1$ and $u_3 = w_3$. Then (7) becomes

$$\begin{array}{cccrr} 1 & 2 & -1 & 0 & 0 \\ 1 & 2 & 0 & 0 & -1 \\ 1 & 3 & -1 & -1 & 0 \\ 1 & 3 & -1 & 0 & 0 \\ 2 & 3 & -1 & 0 & 0 \\ 2 & 3 & 0 & 0 & -1 \end{array} \quad (9)$$

and, after shifting the origin to the position of u_1, the equilibrium configuration is given by

$$\begin{aligned} u_1 &= (0, 0, 0) \\ u_2 &= (\tfrac{1}{2}, \tfrac{1}{6}, \tfrac{1}{6}) \\ u_3 &= (1, \tfrac{1}{3}, \tfrac{1}{3}). \end{aligned} \quad (10)$$

The potential basis vectors are

$$\begin{aligned} b_1 &= u_2 - (1, 0, 0) = (-\tfrac{1}{2}, \tfrac{1}{6}, \tfrac{1}{6}) \\ b_2 &= u_2 - (0, 0, 1) = (\tfrac{1}{2}, \tfrac{1}{6}, -\tfrac{5}{6}) \\ b_3 &= u_3 - (1, 1, 0) = (0, -\tfrac{2}{3}, \tfrac{1}{3}) \\ b_4 &= u_3 - (1, 0, 0) = (0, \tfrac{1}{3}, \tfrac{1}{3}). \end{aligned}$$

As seen in §4, there are symmetries exchanging b_1 with b_2 or b_3 with b_4 or both. Thus, for example, the bases (b_1, b_2, b_3), (b_2, b_1, b_3), (b_1, b_2, b_4) and (b_2, b_1, b_4) all produce identical representations. One combination of six pairwise non-equivalent bases we might use is

$$\begin{aligned} &(b_1, b_2, b_3), \quad (b_3, b_1, b_2), \quad (b_2, b_3, b_1), \\ &(b_2, b_3, b_4), \quad (b_4, b_2, b_3), \quad (b_3, b_4, b_2). \end{aligned}$$

To illustrate the construction of a representation from one of these choices, consider the first triplet (b_1, b_2, b_3), which corresponds to the matrix of base vectors

$$\mathbf{B} = \tfrac{1}{6}\begin{pmatrix} -3 & 1 & 1 \\ 3 & 1 & -5 \\ 0 & -4 & 2 \end{pmatrix}$$

and

$$\mathbf{B}^{-1} = \begin{pmatrix} -3 & -1 & -1 \\ -1 & -1 & -2 \\ -2 & -2 & -1 \end{pmatrix}.$$

We pre-multiply (9) and (10) by $\mathbf{B}^{-1}$ to obtain a representation and an equilibrium placement expressed in the basis $B = (b_1, b_2, b_3)$, namely

$$\begin{array}{cccrr} 1 & 2 & 3 & 1 & 1 \\ 1 & 2 & 2 & 2 & 1 \\ 1 & 3 & 4 & 2 & 3 \\ 1 & 3 & 3 & 1 & 1 \\ 2 & 3 & 3 & 1 & 1 \\ 2 & 3 & 2 & 2 & 1 \end{array} \quad (11)$$

and

$$\begin{aligned} u_1 &= (0, 0, 0) \\ u_2 &= (-2, -1, -1) \\ u_3 &= (-4, -2, -2), \end{aligned} \quad (12)$$

respectively. Now with respect to the new basis, the neighbors of u_1 are two translates of u_2 at $(1, 0, 0)$ and $(0, 1, 0)$ and two translates of u_3 at $(0, 0, 1)$ and at $(-1, -1, -1)$. Sorting lexicographically, the u_3 translates are first, starting with the one at $(-1, -1, -1)$. Thus, $r_2 = u_3 + (3, 1, 1)$ becomes the second vertex representative in our new representation, $r_1 = u_1$ being the first one. The u_2 translates come next, starting with the one at $(0, 1, 0)$, thus we set $r_3 = u_2 + (2, 2, 1)$. In effect, from the neighbors of $r_1 = u_1$, we obtain the following four lines:

$$\begin{array}{ccrrr} 1 & 2 & 0 & 0 & 0 \\ 1 & 2 & 1 & 1 & 2 \\ 1 & 3 & 0 & 0 & 0 \\ 1 & 3 & 1 & -1 & 0. \end{array}$$

We proceed with the two edges emanating from r_2, which we have not seen any translates of yet, *i.e.* with the ones ending in r_3 (or u_2) translates, at positions $(-2, -1, -1)$ and $(-1, -2, -1)$, respectively. The corresponding lines are

$$\begin{array}{ccrrr} 2 & 3 & -2 & -2 & -1 \\ 2 & 3 & -1 & -3 & -1 \end{array}$$

because r_3 is at position $(0, 1, 0)$. After determining and converting to a lattice basis, we obtain the new representation

$$\begin{array}{ccrrr} 1 & 2 & 0 & 0 & 0 \\ 1 & 2 & 1 & 0 & 0 \\ 1 & 3 & 0 & 0 & 0 \\ 1 & 3 & 1 & -1 & 0 \\ 2 & 3 & -2 & 0 & 1 \\ 2 & 3 & -1 & -1 & 1, \end{array}$$

which, incidentally, is already sorted. As an unformated string of numbers, this becomes 1, 2, 0, 0, 0, 1, 2, 1, 0, 0, 1, 3, 0, 0, 0, 1, 3, 1, −1, 0, 2, 3, −2, 0, 1, 2, 3, −1, −1, 1, which is thus the first candidate among six for our canonical form. The smallest of these six is the canonical form.

The canonical form leads directly to the net, so two nets with the same canonical form must be combinatorially isomorphic ('the same'). Conversely, provided only that the algorithm is correctly encoded, the same net always gives the same canonical form, so two nets with different canonical forms are not isomorphic (they are 'different').

6. Realizing an embedding and caveats

Several of the attempts to produce comprehensive lists of nets have been purely combinatorial. Finding good embeddings can be fairly complicated for some of these, mainly because traditional techniques for finding embeddings, which are mostly based on molecular modeling, need a good starting configuration. Otherwise, long relaxation sequences with many restarts may be necessary in order to avoid unfavorable local minima. Random configurations are usually bad choices for starting points because, invariably, structures will be badly entangled, implying many energy barriers between the starting configuration and a favorable minimum.

Equilibrium placements provide a better choice because they minimize the sum of squared edge lengths for a given cell volume, thus usually avoiding unnecessary entanglement. The distribution of edge lengths, however, may be far from uniform, so direct application of realistic potentials may still be costly. It is therefore advisable to first apply a simple refinement procedure. In *Systre*, we use an energy potential based on the variation in edge lengths and the total edge length per volume, thus favoring uniform edge lengths and a large volume-to-average-edge-length ratio. We then use the so-called downhill simplex method (Press *et al.*, 2002) to search for a minimum configuration.

The methods presented here mostly rely on the fact that a vertex can be identified by its position in an equilibrium placement. However, for certain nets, which we have referred to as *unstable* above, vertices will *collide* in the sense that they have identical equilibrium positions. An example of a net in which collisions occur is illustrated in Fig. 3. Such situations are easily detected so, provided implementations are correct, there will be no danger of incorrect results without notice.

Apparently, collisions rarely occur in nets extracted from real crystal structures. We processed the complete list of known zeolite framework types (Baerlocher *et al.*, 2001) and several hundred additional nets compiled by the second author without ever encountering one. Many nets generated by combinatorial means, however, do have collisions, so they may not work properly with the current version of *Systre*. With slightly more sophisticated algorithms, most of these will probably be handled fairly efficiently, although the general problem of recognizing nets is closely related to that of recognizing finite graphs. For the complexity of the latter, it is not yet known whether it lies in the exponential or polynomial range.

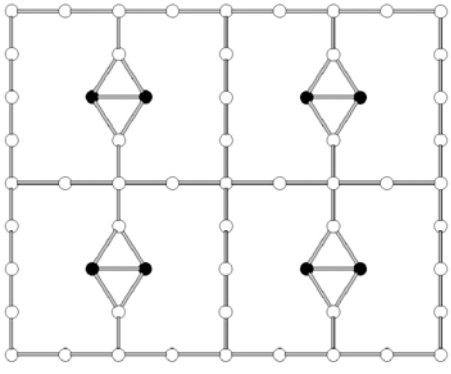

Figure 3
A net with vertices that collide in pairs in an equilibrium placement (*i.e.* with barycentric coordinates). Pairs that collide are shown as filled circles.

It was mentioned earlier that the symmetry group computed by our methods is the maximal achievable crystallographic symmetry group of a net. Indeed, in the absence of vertex collisions, every combinatorial symmetry of a net is realized by a distinct crystallographic symmetry. If vertex collisions occur, however, some symmetry that moves a vertex may actually move it to a colliding one and thus may in fact correspond to the identity transformation.

Even without collisions, the symmetry group computed by *Systre* may be larger than expected. Thus, the symmetry group (*Cmmm*) of the moganite net discussed in the previous sections shows that there are only three vertices in the primitive cell. However, one vertex is constrained by symmetry to have a planar coordination and, if this net is to serve as the *T* net in a compound TX_2 with tetrahedral coordination, the symmetry group must be lowered for example to *Ibam*, a k_2 subgroup with $\mathbf{c}' = 2\mathbf{c}$, as in BeH_2 (Smith *et al.*, 1988). A similar situation arises in the germanate zeolite ASV (ASU-7), in which the underlying Ge net has symmetry group $P4/mmm$ but again to accommodate a non-planar coordination the symmetry group must be reduced to *e.g.* $P4/mmc$ with $\mathbf{c}' = 2\mathbf{c}$ (O'Keeffe & Yaghi, 1999).

If, in a four-coordinated net such as that of moganite, every vertex is replaced by a tetrahedron of vertices, the ideal symmetry group remains the same but can only be attained if some tetrahedra are represented as squares with diagonal edges (*i.e.* planar). We use a different example for illustration of this phenomenon: that of the $CdSO_4$ net (Delgado-Friedrichs *et al.*, 2003). Fig. 4 shows two examples, with symmetry group *Ama*2 and $P4_122$, of structures derived from the $CdSO_4$ net by replacing vertices by tetrahedra. In each case, *Systre* derives the symmetry group $P4_2/mmc$ and with the tetrahedra collapsed to squares with pairs of intersecting diagonal edges that lie in a mirror plane as shown in Fig. 4 (realizations with intersecting edges are not valid embeddings). Notice that the

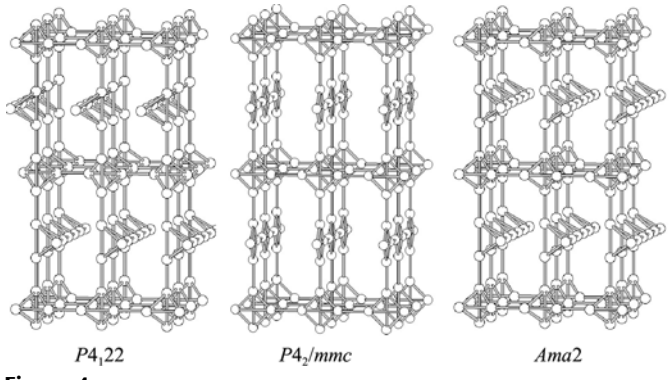

Figure 4
Three realizations of a net with combinatorial symmetry $P4_2/mmc$. The one in the center with edges intersecting is not considered an acceptable embedding (note that the apparent non-intersection of the edges corresponding to diagonals of squares is an artifact of the drawing program used).

two tetrahedral structures with symmetry group *Ama*2 and $P4_122$, have the same topology as determined by *Systre* (this can be checked by calculating other invariants such as coordination sequences and vertex symbols), although they cannot be interconverted without breaking bonds. Notice also that, although the $P4_122$ structure is topologically chiral, it is not *intrinsically* chiral as the embedding with symmetry group *Ama*2 demonstrates. However, if Systre finds a chiral combinatorial symmetry, the net must be intrinsically chiral; we note that the problem of deciding whether a molecular graph is chiral remains a non-trivial problem (*e.g.* Flapan, 2000).

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