Rigid, flexible and impossible zeolite and related structures

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The flexibility or otherwise of periodic tetrahedral TX$_2$ frameworks formed by corner-sharing regular TX$_4$ tetrahedra is discussed. In particular, when T–X–T angle constraints are included, a suitable embedding can often only be found, if at all, in an symmetry less than the maximum possible for that topology. Examples illustrating this are adduced.

1. Introduction

Zeolites are immensely valuable materials that find wide use in the chemical industry, and considerable effort has been made over the past 50 years both to synthesize new materials and to predict new possibilities. Their frameworks are composed of vertex-sharing TX$_4$ tetrahedra with overall stoichiometry TX$_2$. Here, T is an atom such as Si, and X is usually an O atom. Similar frameworks are the basis for minerals such as quartz and feldspar that make up the bulk of the Earth’s crust. In particular, in silicates, the X$_4$ tetrahedra are very nearly regular, and in what follows the primary structural constraint is taken as just that: regular tetrahedra of such a size that the T–X bond length has its preferred value. With appropriately sized tetrahedra, the T atom automatically fits in a unique site in the tetrahedron, so its existence is generally ignored in what follows.

I, however, consider an additional constraint: that of the T–X–T angle. Generally, depending on the chemical identity of the atoms, this has a preferred value: e.g. about 145° for Si–O–Si and Al–O–Si, and 130° for Ge–O–Ge [1]. In identifying potential zeolite frameworks, it will therefore be asked first: which can be made with regular tetrahedra? Then of these, it will be asked: can the T–X–T angles be made equal? And then, if so, to what angle. Thus, if all angles can be made equal (or ‘nearly’ equal) to 145°, then the structure is a candidate for a silica zeolite; if equal (or ‘nearly’ equal) to 130°, then a candidate for a germanate zeolite.
Figure 1. The net $\text{fnm}$ (a) in maximum symmetry $Ia\bar{3}d$, (b) with symmetry $I\bar{4}3d$ an equal edge lengths.

The T structure will be an embedding of a six-coordinated periodic net. Here, a net is a simple connected graph [2]. In what follows, the net is considered to be crystallographic, i.e. the automorphism group of the graph is isomorphic to a crystallographic group. This is the case for all known zeolite nets. The net is also a sphere packing net, which means that it has an embedding in which the edges correspond to the equal shortest distances between vertices (so, in the corresponding sphere packing, the centres of equal-diameter spheres are at the vertex positions, and contacts correspond to the mid-points of edges).

The topology of zeolites (the framework type) is usually characterized by the four-coordinated T net, in which –X– links serve as edges. For known zeolites, the framework type is assigned a symbol such as $\text{FAU}$ for the framework of faujasite-structured zeolites. Other nets are assigned symbols in the reticular chemistry structure resource (RCSR) database [3], these are written in lower case as $\text{fau}$ (generally, but not always, RCSR symbols and zeolite framework symbols for the same net use the same set of letters). The net of the X atoms, with which we are primarily concerned, is the edge net of the four-coordinated net. This is derived by placing new vertices in the centre of the original edges and constructing a complete graph (a tetrahedron) from the new vertices around each original vertex. The original graph is then deleted. Generally, in the RCSR database, these are identified by an extension $-e$ as in $\text{fau-e}$.

A recent review [4] of what is known about periodic nets may be consulted for details and references. Here, some relevant points are briefly touched on.

Owing to extensive efforts of Werner Fischer and co-workers, almost all (some monoclinic examples may be missing) vertex-transitive sphere packing nets are known (see [4] for references therein). The number of these is about 1000, the exact number depends on what one considers a new sphere packing. The RCSR generally does not include $z$-coordinated sphere packings that have more than $z$ contacts in their maximum symmetry embeddings. On the other hand, some $z$-coordinated sphere packings may have fewer than $z$ contacts in a maximum symmetry embedding. This is relevant to the subsequent discussion, so a simple example is adduced here.

The five-coordinated net $\text{fnm}$ (figure 1) has symmetry $Ia\bar{3}d$, and vertices are in the special positions 1/8, 1/8, 1/8, etc. There are two kinds of edge and just one variable parameter, the cubic cell edge, so the edge lengths cannot be made equal—they are in fixed ratio $\sqrt{2}/3$. However, if the symmetry is lowered to $I\bar{4}3d$, then the vertices are now $x$, $x$, $x$, etc., and with $x = 0.0366$ all edges are equal. In the search for suitable zeolite nets, the hard part at present is finding the correct descent in symmetry to find an optimal embedding, if it exists. The problem seems difficult; space groups are of infinite order, and thus have infinitely many subgroups. Here, I am content simply to cite some examples, mostly from my earlier work, that illustrate the general problem.

For the X nets of zeolites in symmetry $P1$, generally, all edges can be made equal. Without loss of generality, one vertex can be placed at 0, 0, 0, a second at $x$, 0, 0 and a third at $x$, $y$, 0,
so that for \( N \) vertices in the unit cell there are \( 3N - 6 \) coordinates. Including the six unit cell parameters, there are \( 3N \) degree of freedom (d.f.), equal to the number of edges. However, the system of equations for the edge lengths is quadratic, so there is no guarantee of a real solution in every case.

Also of interest is that we (think we) know all the edge-transitive sphere packings. These are of special interest to designed synthesis of certain classes of materials [5]. Nets related to those of the four-coordinated edge-transitive sphere packings are discussed first.

2. Edge-transitive four-coordinated nets

The RCSR database has 13 edge-transitive four-coordinated nets. Only six of these are suitable for tetrahedral coordination at the vertices in their maximum symmetry embeddings. For example, if the vertex is on a centre of inversion, then it cannot have tetrahedral coordination (I return to this point later). If these six are taken as the T net of a TX\(_2\) framework, then the X net will be vertex transitive and of necessity all T–X–T angles will be equal. The net will be the edge net of the original, each is considered in turn.

(a) \( \text{qtz-e} \)

This is the anion net of the familiar quartz structure with symmetry \( P6_22 \). The vertices are in positions \( x, 2x, 1/2, \) etc., and there are three independent edge lengths; as there are two unit cell parameters (\( a \) and \( c \) of the hexagonal cell), the three edges can be made equal to the desired value. But, now the T–X–T angle is fixed at 155.6°. Lowering the symmetry to \( P3_221 \) puts the vertices in general positions \( x, y, z, \) and there are now four edges. But now setting the edges equal to the desired value, there is a remaining degree of freedom allowing the tetrahedra to undergo concerted rotations and reduce the T–X–T angle to a continuous range of smaller values. This is the familiar \( \beta \rightarrow \alpha \) transition in quartz fully described in textbooks [6].

(b) \( \text{sod-e} \)

This is the anion net of the sodalite framework [6]. The symmetry is \( Im\bar{3}m \), and vertices are in positions \( 0, y, y, \) etc., and together with the cell edge \( a \), the 2 d.f. allow fixing the two edge lengths. But, again, the TX–T angle is fixed, this time at 160.6°. Lowering the symmetry to \( P3_221 \) puts the vertices in general positions \( x, y, z, \) and there are now four edges. But now setting the edges equal to the desired value, there is a remaining degree of freedom allowing the tetrahedra to undergo concerted rotations and reduce the T–X–T angle to a continuous range of smaller values. This range of flexibility accounts for the fact that, as well in silicate minerals, such as sodalite and ultramarine, the sodalite framework is also found in tetrahedral sulfides and chlorides, for which T–X–T angles are typically close to 110°.

(c) \( \text{dia-e} \) (also assigned the symbol crs)

This structure is ubiquitous in crystal chemistry [1] (figure 2). The symmetry is \( Fd\bar{3}m \), and the X vertices are in invariant positions on inversion centres at 0, 0, 0, etc. The T vertices are also at fixed positions at sites of tetrahedral symmetry—indeed, it is the only TX\(_2\) framework with this property. In the maximum symmetry, there is only 1 d.f. (the unit cell edge \( a \)) which determines the scale. The T–X–T angles are fixed at 180°. Three lower-symmetry variants in which the T–X–T angles are all equal but variable have been described [1]. These are

(i) \( I42d \). X vertices in univariant positions \( x, 1/4, 1/8, \) etc., so three variables when combined with the tetragonal cell edges \( a \) and \( c \). There are two independent edge lengths and the T–X–T angles (necessarily all equal) can take any value from 180° to 109.5° at which point the nearest intertetrahedral X . . . X distances become equal to the
Figure 2. Fragments of the crs net. (a) A 10-tetrahedron unit with T–X–T = 180°. (b) The same viewed down a fourfold axis. (c) The same unit with T–X–T = 145° and $\overline{I}42d$ symmetry. (d) The same unit with T–X–T = 145° and $P4_122$ symmetry.

intradetrahedral distances. The X arrangement is then the 12-coordinated structure of cubic closest packing.

(ii) $P4_1212$. X vertices in one set of general positions $x, y, z$, etc., so now five variables. There are four edge lengths, so, again, the unique T–X–T angle is variable. This is the structure found in the silica polymorph $\alpha$-cristobalite.

(iii) $Pna2_1$. In this orthorhombic space group, there are three cell edges $a, b, c$ and, the only orbits are the general positions $x, y, z$. There are now two sets of X vertices, but only eight variables as for this polar symmetry one vertex can be set at $x, y, 0$. There are six independent edges and two independent T–X–T angles, which can be set equal to a variable angle. When T–X–T = 109.5°, the X arrangement is the 12-coordinated structure of hexagonal closest packing.

(d) lcs-e

This is an interesting, but little-known structure. The symmetry is $Ia\overline{3}d$. The X vertices are in positions $1/8, y, y – 1/4$. There are two edges which are equal for $y = 0.2835$, at which point the T–X–T angle is fixed at 150.0°. No lower-symmetry variant has been described.

(e) ana-e

This structure corresponds to the anion array in the natural aluminosilicate zeolite analcime (or analcite). The symmetry is $Ia\overline{3}d$. The X vertices are in one set of general positions $x, y, z$. There are four edges which, when made equal, constrain the T–X–T angle to be equal to 148.8°, conveniently close to the preferred value for aluminosilicates. No lower-symmetry variant has been described. I think there may not be one with variable T–X–T angle.

(f) lcv-e

This is an example of a framework that cannot be made with regular tetrahedra and maximum symmetry. The symmetry is $I4_132$ with X vertices at $1/8, y, 1/4 – y$, etc. There are three edges, but
only two variables, and the edges cannot be made equal. Reducing the symmetry to $I\overline{2}13$ puts the
$X$ vertices in one set of general positions, so there are now four variables, but also four edges, and
if these are set equal, then the $T$–$X$–$T$ angle is fixed at $109.5^\circ$. At this point, each $X$ vertex has nine
equidistant neighbours.

3. The moganite polymorph of silica

Moganite is a little-known, yet of wide-spread occurrence, polymorph of silica [7]. The four-
coordinated net, $\text{mog}$, has symmetry $Cmmm$. In an embedding, in this maximum symmetry, one
of the vertices lies on a site of symmetry $mmm$, and in the corresponding edge net (figure 3), the
‘tetrahedron’ becomes a square with intersecting diagonal edges [4]. In order to have tetrahedral
coordination at that site one must go to a $k$ subgroup (one that has lost some translational
symmetry), namely $Ibam$. Now, there are two vertices in the $X$ net (hence two $T$–$X$–$T$ angles) and
seven $X$–$X$ distances. There are 8 d.f., so the $T$–$X$–$T$ angles can be made equal (to $161^\circ$). In low
temperature moganite, the symmetry is further lowered to $I\overline{2}/a$. There are now three kinds of $X$
vertex in general positions ($x$, $y$, $z$) and four unit cell parameters for the monoclinic cell, so 13 d.f.
There are 10 independent $X$–$X$ distances, so the three $T$–$X$–$T$ angles can now be set to any one of
a range of angles, for example $145^\circ$. In the reported structure of moganite $\text{SiO}_2$, the angle is close
to this [8,9].

4. Some other zeolites

Many of the low-density zeolite nets are simple tilings. Simple polyhedra are convex polyhedra with
all three-valent vertices. Simple tilings are those of simple polyhedra in which two tiles meet at a
face, three at an edge and four at a vertex (in each case, the minimum number). There are exactly
nine uninodal simple tilings (actually determined as their dual structures, nine isohedral tilings
by tetrahedra) [10]. Six of these are nets of known aluminosilicate zeolites, two others have three
rings in which case the maximum $T$–$X$–$T$ angle for regular tetrahedra is $130.5^\circ$ (actually for one of
these two the $T$–$X$–$T$ angle is fixed at $109.5^\circ$ and is known as a sulfide with zeolite code $\text{RWY}$).

The other uninodal simple tiling not known as a zeolite net is $\text{wse}$ (identified as $W^8$ in
[6]). In $\text{wse-e}$ (symmetry $Im\bar{3}m$), there are four $X$ atoms and six independent $X$–$X$ edges for 10
constraints. However, including the cubic cell edge, there are only 8 d.f. With regular tetrahedra,
then the closest one can get to equal $T$–$X$–$T$ angles is $133.8^\circ$ and $168.7^\circ$ [6]. As far as I know,
lower-symmetry embeddings have not been explored.

By contrast, for faujasite (economically, the most important aluminosilicate zeolite) with
exactly the same number of constraints for $\text{fau-e}$ as for $\text{wse-e}$, the four $T$–$X$–$T$ angles can
be brought into the range $140.7^\circ$–$144.0^\circ$ (this is slightly different from the values quoted in
The zeolite framework MTN, also known as the type II clathrate structure, is of interest as in the maximum symmetry embedding of mtn-e, Fd3m, there are four vertices and seven X–X distances, and 6 d.f., and indeed in that symmetry not all X–X distances can be made equal. In the maximal subgroup $I4_1/amd$, there are seven vertices, 16 X–X distances and 15 d.f., so again the tetrahedra cannot be made regular. Descending further to a next maximal subgroup $I4_1/a$, there are nine vertices, 26 X–X distances and 27 d.f., so now all edges can be made equal. This is in fact the symmetry of the observed all-silica MTN [11] in which the T–X–T angles are not equal but in an acceptable range (149–172°) for a silicate.

As a last example, I cite a group of zeolites with four-coordinated nets that include groups of eight vertices with the topology of a cube (in zeolite parlance, this is a double four-ring, D4R) [13]. In every case, the discussion refers to embeddings with regular tetrahedra (all X–X distances equal). In ACO (RCSCR symbol pcb) the ideal symmetry Im3m. In an embedding with this symmetry, the two T–X–T angles are fixed at 180° and 148.4°. Lowering the symmetry to $P4/ mmc$ allows all t–X–T angles to be 148.4°, suitable to silicates. Further lowering the symmetry to either $Pnmn$ or to $Cccm$ allows the T–X–T angles to remain equal and vary in the range 129.6–148.4°. The lower value is suitable for germanates and ACO structures are known for both silicates and for germanates. A similar situation holds for the topology AST with the same values of T–X–T angles. In the maximum symmetry of $Fm3m$, the angles are fixed at the unequal values. In an embedding in $I4/m$, the angles can be made equal to 148.4°, and in $I2/morP2/m$, the range is 129.6–148.4°. AST structures are also found is silicates and germanates.

In the LTA framework (a uninodal simple tiling discussed above), the smallest range of T–X–T angles at maximum symmetry is 145–154°, and this topology is known only for aluminosilicate.

Finally, in ASV, the topological symmetry of the net is $P4/mnm$, but with this symmetry, just like the moganite case discussed above, one vertex is in a site of symmetry mnm, precluding tetrahedral TX₄ groups at this point, and the symmetry has to be lowered by loss of translations to a doubled cell with symmetry $P4/mmc$. Finally, lowering the symmetry to $Pccm$ allows the T–X–T angles to be made equal, at which point they are 131.1°. This is just suitable for a germanate zeolite, and the ASV topology is known only for a germanate. In this example, there are nine X–X distances, three X vertices (so three T–X–T angles) and 11 d.f.

5. Conclusion: questions and speculations

The problem of finding the optimum symmetry (or symmetries) for a given framework seems at first sight formidable. For a given net, it is straightforward using the computer program SYSTRE to find the combinatorial symmetry, which is isomorphic to the space group of a maximum symmetry embedding [14]. For most of the examples adduced here, the optimum symmetry as a zeolite net is a subgroup of this. But then to find the appropriate subgroup can be tedious as a space group has many t (translation preserving) subgroups, because an orthorhombic subgroup, for example, can occur in different orientations. Thus, $Pmn2$, $Pm2mand P2nm$ are all subgroups of $Pnmn$. And if translations are deleted, then there are infinitely many subgroups.

However, in all the examples examined in which lowering symmetry improved the accommodation of angle constraints, the T atom sites were in special positions (i.e. had non-trivial site symmetry). It would be very nice if the inverse were true, i.e. that when all the T sites

[6])
have only trivial symmetry, there is no improvement to be gained in the ratio of degrees of freedom to constraints by going to lower symmetry. This would make the general problem much more tractable.

It appears that most zeolite frameworks have additional degrees of freedom once the constraints of equal edges are satisfied [15]. But, of these, only a small subset can be made to have all T–X–T angles equal. And for only a small subset of those can the T–X–T angle be variable. And of those there is no known example of a framework that has additional degrees of freedom, i.e. that has more degrees of freedom than distance and angle constraints.

Acknowledgements. I am indebted to Mike Treacy and Colby Dawson for many enlightening discussions on zeolites, periodic nets and related topics.

Funding statement. Support of this work by the US National Science Foundation (grant no. DMR-1104798) is gratefully acknowledged.

References