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Deformations of Crystal Frameworks

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Abstract

We apply our deformation theory of periodic bar-and-joint frameworks to tetrahedral crystal structures. The deformation space is investigated in detail for frameworks modelled on quartz, cristobalite and tridymite.

Keywords: periodic frameworks, deformations, flexibility, silica polymorphs.

Introduction

In this paper we present specific applications of our general deformation theory of periodic frameworks [BS].

Considerations related to *framework flexibility* appear already in the early structural investigations based on X-ray crystallography [G1, G2, P1, P2]. For framework materials, envisaged as corner sharing polyhedra, an intuitive notion of a 'coordinated tilting' of the polyhedra is used in classifying similar structures [Gla, M] or in studies of thermal and pressure effects. A most important area of theoretical and experimental studies where geometric models of deforming frameworks have been implicated is that concerned with *displacive phase transitions* [GD, Dol, D].

Regarding the use of geometrical facts, it should be observed that, for most framework structures, only a confined sample of geometrical possibilities has been explored in the literature, typically one-parameter families which are intuitively 'accessible'. The deformation theory developed in our paper [BS] shows that one may expect, in general, a rich and diverse geometry. The present undertaking describes the deformation spaces for tetrahedral periodic frameworks modeled on *quartz, cristobalite and tridymite.*

1 The quartz framework

The ideal structure considered here is made of congruent regular tetrahedra. The oxygen atoms would correspond with the vertices, each oxygen being shared by two tetrahedra. The silicon atoms should be imagined at the centers of the tetrahedra. We shall examine all the geometric deformations of the periodic framework described in Figure 1, without concern for self-collision or any prohibition of a physical nature.

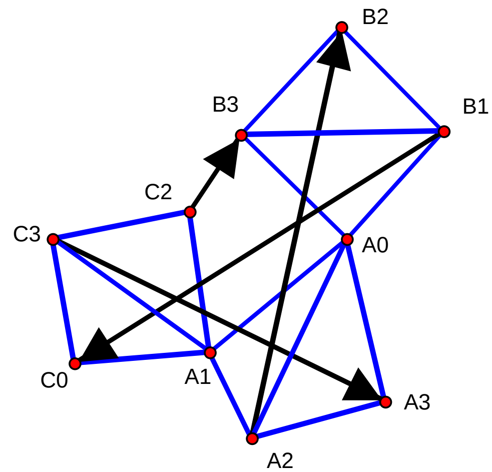

Figure 1: A fragment of the tetrahedral framework of quartz. The periodicity lattice is generated by the four marked vectors, which must maintain a zero sum under deformation. The full framework is obtained by translating the depicted tetrahedra with all periods.

Equivalence under Euclidean motions is eliminated by assuming the tetrahedron marked $A_0A_1A_2A_3$ as fixed. Since all edges maintain their length, the positions of the two tetrahedra which share the vertices A_0 and A_1 are completely described by two orthogonal transformations R_0, respectively R_1 as follows: R_0 fixes A_0 and takes A_i to B_i, $i \neq 0$, while R_1 fixes A_1 and takes A_j to C_j, $j \neq 1$. The figure, by depicting only the 'visible' edges, implies that both R_0 and R_1 are orientation reversing, that is, as orthogonal matrices $-R_0, -R_1 \in SO(3)$.

If we denote the edge vectors $A_i - A_0$ by $e_i, i = 1, 2, 3$, we have:

$$B_3 - C_2 = R_0 e_3 - (e_1 + R_1(e_2 - e_1))$$

$$A_3 - C_3 = e_3 - (e_1 + R_1(e_3 - e_1))$$

$$B_2 - A_2 = R_0 e_2 - e_2$$

$$C_0 - B_1 = e_1 - R_1 e_1 - R_0 e_1$$

It follows that the dependency condition of a zero sum for these four generators of the periodicity lattice takes the form

$$R_1(e_1 - e_2 - e_3) - R_0(e_1 - e_2 - e_3) = e_1 + e_2 - e_3 \tag{1}$$

Under our regularity assumptions, the three vectors $R_1(e_1 - e_2 - e_3)$, $R_0(e_1 - e_2 - e_3)$ and $(e_1 + e_2 - e_3)$ have the same length and form an equilateral triangle. This restricts $R_0(e_1 - e_2 - e_3)$ to the circle on the sphere of radius $||e_1 - e_2 - e_3||$ (which corresponde with an angle of $2\pi/3$ with $e_1 + e_2 - e_3$). Thus, $-R_0 \in SO(3)$ is constrained to a surface, which is differentiably a two-torus $(S^1)^2$.

For each choice of $-R_0$ on this torus, $R_1(e_1 - e_2 - e_3)$ is determined by (1), hence $-R_1$ is restricted to a circle S^1 in $SO(3)$. It follows that

Theorem 1 *The deformation space of the ideal quartz framework is given by a three dimensional torus $(S^1)^3$ minus the degenerate cases when the span of the four vectors is less than three dimensional.*

2 The cristobalite framework

The case of the 'ideal β cristobalite' structure illustrated in Figure 3 is already covered in [BS]. The periodicity group of the framework is give by all the translational symmetries of the ideal crystal framework. As a result, there are $n = 4$ orbits of vertices and $m = 12$ orbits of edges.

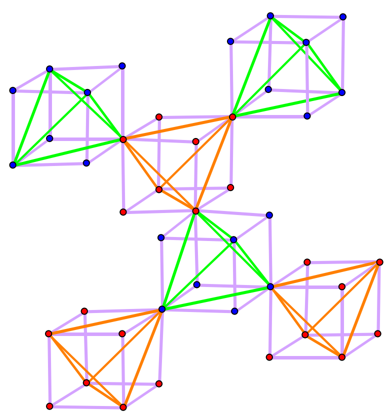

Figure 2: The ideal cristobalite framework (aristotype). The framework is made of vertex sharing regular tetrahedra. Cubes are traced only for suggestive purposes regarding symmetry and periodicity. See also Figure 3.

Adopting the notations of Figure 2, we may assume the tetrahedron $Os_1s_2s_3$ as fixed and parametrize the possible positions of the other tetrahedon by a rotation around the origin O.

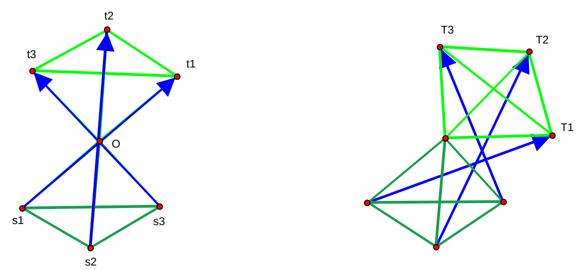

Figure 3: Deforming the ideal cristobalite framework. The periodicity lattice is generated by the three vectors $\gamma_i = t_i - s_i$ which vary as the framework deforms.

Theorem 2 *The deformation space of the ideal high cristobalite framework is naturally parametrized by the open set in $SO(3)$ where the depicted generators remain linearly independent.*

3 The tridymite framework

The tetrahedral framework (G, Γ) of tridymite is depicted in Figure 4. We consider the ideal case made of regular tetrahedra. The quotient graph has $|V/\Gamma| = 8$ and $|E/\Gamma| = 24$. All deformations can be described by three orthogonal transformations (matrices) R_0, R_1, R_2 acting with centers at $O, O1$ and respectively $O2$. With O as the origin and the tetrahedron $OD_1E_1O_1$ assumed fixed, we put:

$$O_1 = f_0, \quad D_1 = f_1 \quad \text{and} \quad f_1 = f_2$$

Then, our orthogonal transformations are determined by the following relations:

$$O_2 = R_0 f_0, \quad D_2 = R_0 f_1 \quad \text{and} \quad f_2 = R_0 f_2$$

$$A_1 = f_0 + R_1(f_1 - f_0), \quad B_1 = f_0 + R_1(f_2 - f_0), \quad C_1 = f_0 - R_1 f_0$$

$$A_2 = R_0 f_0 + R_2 R_0 (f_1 - f_0), \; B_2 = R_0 f_0 + R_2 R_0 (f_2 - f_0), \; C_2 = R_0 f_0 - R_2 R_0 f_0$$

As a result, the two linear dependence relations between the six depicted periods take the form:

$$(I - R_0 - R_1 + R_2 R_0) f_i = 0, \quad i = 1, 2 \tag{2}$$

where I denotes the identity. We note that the ideal high tridymite structure (the *aristotype*) corresponds to $R_0 = -I$ and $R_1 = R_2$ the reflection in the plane *span*(f_1, f_2)).

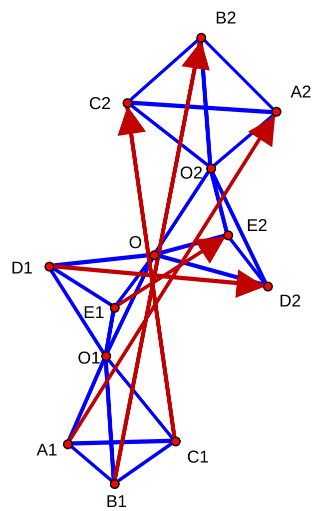

Figure 4: The tetrahedral framework of tridymite. The periodicity lattice is generated by the marked vectors, subject to the relations $(C_2-C_1)+(D_2-D_1) = (A_2 - A_1)$ and $(C_2 - C_1) + (E_2 - E_1) = (B_2 - B_1)$.

We shall describe the deformation space in a neighbourhood of this high tridymite structure. We put $-R_0 = Q$, $R_1 = Q_1$ and $-R_2R_0 = Q_2$, so that (2) becomes

$$I + Q = Q_1 + Q_2 \quad \text{on} \quad span(f_1, f_2) \tag{3}$$

with $Q, -Q_1, -Q_2 \in SO(3)$. Since the orthogonal transformations Q, Q_1, Q_2 are completely determined by their values on two vectors e_1, e_2 of a Cartesian frame with $span(e_1, e_2) = span(f_1, f_2)$, we have to solve the system

$$e_i + Qe_i = Q_1e_i + Q_2e_i \quad i = 1, 2 \tag{4}$$

where we assume $Q \in SO(3)$ given in a neighbourhood of the identity, and look for solutions Q_1, Q_2.

We may interpret this system as a problem about a *spherical four-bar mechanism* in the following way. All the vectors implicated in (4) are unit vectors and can be depicted as points on the unit sphere S^2. For a given Q, we mark by M_i the midpoint of the spherical geodesic segment $[e_i, Qe_i]$ and trace the circle with center M_i and diameter $[e_i, Qe_i]$. This is illustrated in Figure 5.

It is an elementary observation that any solution Q_1e_i and Q_2e_i determines diameters of the corresponding circles for $i = 1, 2$, with the two geodesic arcs $[Q_ke_1, Q_ke_2]$, like $[e_1, e_2]$ and $[Qe_1, Qe_2]$, of length $\pi/2$. Thus, the two spherical quadrilaterals with vertices at e_1, Qe_1, Qe_2, e_2 and respectively Q_1e_1, Q_2e_1,

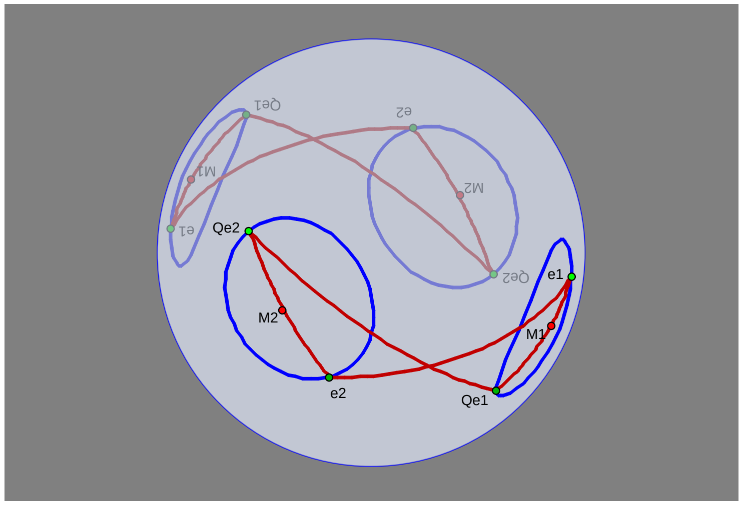

Figure 5: The spherical four-bar mechanism associated to the system (4).

Q_2e_2, Q_1e_2 are two configurations of the same four-bar mechanism and moreover, the distance between the midpoints of the opposite edges represented by diameters is the same.

It follows from the theory of the spherical four-bar mechanism that, for a generic Q near the identity of $SO(3)$, the abstract configuration space is made of two loops which correspond by reflecting the corresponding realizations. Each loop component has two configurations with the prescibed distance $[M_1M_2]$. Thus, there are four configurations with the prescribed distance.

We observe that if we replace Q_1 by Q_2 and Q_2 by Q_1 in the labeling of the vertices of a realization, the orientation is reversed, hence the configuration belongs to the other component. Thus, the two obvious solutions of (4), namely

$$Q_1e_i = e_i,\ Q_2e_i = Qe_i \quad \text{and} \quad Q_1e_i = Qe_i,\ Q_2e_i = e_i, \quad i = 1, 2$$

correspond with configurations on the two different loop components, as do the remaining two, which are also paired by relabeling. This discussion shows that all four solutions are obtained from the quadrilateral e_1, Qe_1, Qe_2, e_2 and its reflection in the geodesic $[M_1, M_2]$, by the two relabelings with Q_1 and Q_2 possible in each case.

In Figure 6 we have depicted the quadrilateral e_1, Qe_1, Qe_2, e_2 as $A_1B_1B_2A_2$, with reflection in $[M_1M_2]$ marked as rA_1, rB_1, rB_2, rA_2. Then,, the solutions $(Q_1e_1, Q_1e_2, Q_2e_1, Q_2e_2)$ of the system (4) are the following four solutions: (A_1, A_2, B_1, B_2), (B_1, B_2, A_1, A_2), (rA_1, rA_2, rB_1, rB_2) and (rB_1, rB_2, rA_1, rA_2).

We may summarize our result as follows.

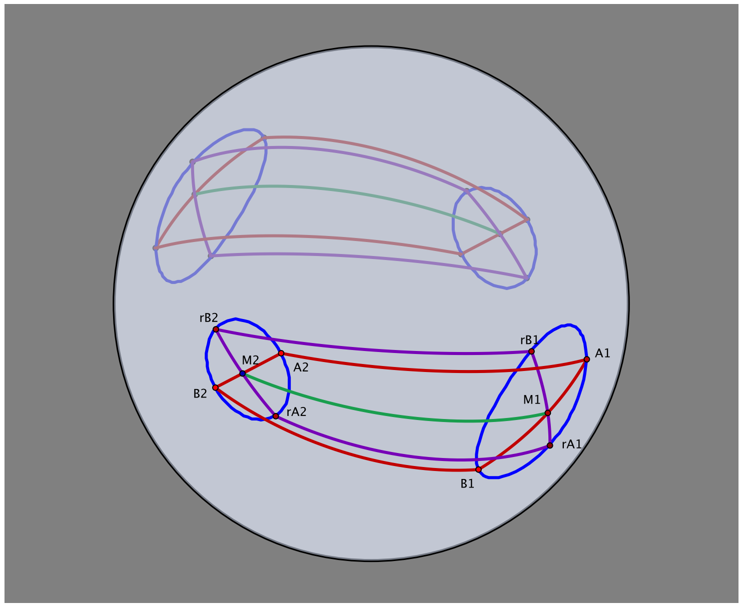

Figure 6: Spherical four-bar mechanism and reflection in $[M_1, M_2]$.

Theorem 3 *The deformation space of the tridymite framework is singular in a neighbourhood of the aristotype and can be represented as a ramified covering with four sheets of a three-dimensional domain. There is a natural $Z_2 \times Z_2$ action on this covering which fixes the aristotype framework.*

Indeed, the two involutions, inverting the labeling and reflecting in $[M_1, M_2]$, commute ang give a $Z_2 \times Z_2$. action on the covering. The dimension of the tangent space at the aristotype framework is computed from the linear version of (4) and is six.

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