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Deformations of crystal frameworks

Ciprian S. Borcea and Ileana Streinu

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:

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

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

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

$$C_0 - B_1 = e_1 - R_1e_1 - R_0e_1$$

It follows that the dependency condition of a zero sum for these four generators of the periodicity lattice takes the form
\[ R_1(e_1 - e_2 - e_3) - R_0(e_1 - e_2 - e_3) = e_1 + e_2 - e_3 \]  \hspace{1cm} (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 corresponds 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 given 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.](image-url)

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 tetrahedron by a rotation around the origin \( O \).
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 $(G, \Gamma)$ 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 $O, O_1$ and respectively $O_2$. 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:

$$O_2 = R_0f_0, \quad D_2 = R_0f_1 \quad \text{and} \quad f_2 = R_0f_2$$

$$A_1 = f_0 + R_1(f_1 - f_0), \quad B_1 = f_0 + R_1(f_2 - f_0), \quad C_1 = f_0 - R_1f_0$$

$$A_2 = R_0f_0 + R_2R_0(f_1 - f_0), \quad B_2 = R_0f_0 + R_2R_0(f_2 - f_0), \quad C_2 = R_0f_0 - R_2R_0f_0$$

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

$$(I - R_0 - R_1 + R_2R_0)f_i = 0, \quad i = 1, 2 \quad (2)$$

where $I$ denotes the identity. We note that the ideal high tridymite structure (the aristotype) corresponds to $R_0 = -I$ and $R_3 = R_2$ the reflection in the plane $\text{span}(f_1, f_2)$.
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

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

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 $\text{span}(e_1, e_2) = \text{span}(f_1, f_2)$, we have to solve the system

$$e_i + Q e_i = Q_1 e_i + Q_2 e_i \quad i = 1, 2$$

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 $[e_i, Q e_i]$ and trace the circle with center $M_i$ and diameter $[e_i, Q e_i]$. This is illustrated in Figure 5.

It is an elementary observation that any solution $Q_1 e_i$ and $Q_2 e_i$ determines diameters of the corresponding circles for $i = 1, 2$, with the two geodesic arcs $[Q_k e_1, Q_k e_2]$, like $[e_1, e_2]$ and $[Q e_1, Q e_2]$, of length $\pi/2$. Thus, the two spherical quadrilaterals with vertices at $e_1, Q e_1, Q e_2, e_2$ and respectively $Q_1 e_1, Q_2 e_1$, $Q_1 e_2, Q_2 e_2$.
Figure 5: The spherical four-bar mechanism associated to the system (4).

$Q_2 e_2, Q_1 e_2$ 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 prescribed distance $[M_1 M_2]$. 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

\[ Q_1 e_i = e_i, \quad Q_2 e_i = Q e_i \quad \text{and} \quad Q_1 e_i = Q e_i, \quad Q_2 e_i = e_i, \quad i = 1, 2 \]

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 $e_1, Q e_1, Q e_2, e_2$ 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 5 we have depicted the quadrilateral $e_1, Q e_1, Q e_2, e_2$ as $A_1 B_1 B_2 A_2$, with reflection in $[M_1 M_2]$ marked as $r A_1, r B_1, r B_2, r A_2$. Then, the solutions $(Q_1 e_1, Q_1 e_2, Q_2 e_1, Q_2 e_2)$ of the system (4) are the following four solutions:

$(A_1, A_2, B_1, B_2), (B_1, B_2, A_1, A_2), (r A_1, r A_2, r B_1, r B_2)$ and $(r B_1, r B_2, r A_1, r A_2)$.

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 $\mathbb{Z}_2 \times \mathbb{Z}_2$ action on this covering which fixes the aristotype framework.

Indeed, the two involutions, inverting the labeling and reflecting in $[M_1, M_2]$, commute and give a $\mathbb{Z}_2 \times \mathbb{Z}_2$ 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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