Deformations of crystal frameworks

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Workshop on Rigidity and Symmetry
Toronto, Fields Institute , October 17-21, 2011

Outline:

1. Periodic frameworks: review of some fundamental notions

from Borcea, C.S. and Streinu, I.:
Periodic frameworks and flexibility, Proc. Roy. Soc. A 466 (2010), 2633-2649.

2. Frameworks of the silica polymorphs: cristobalite, quartz and tridymite

3. Geometric deformations of crystal frameworks

3.1 Cristobalite

3.2 Quartz

3.3 Tridymite

1. Periodic frameworks

Definitions:.

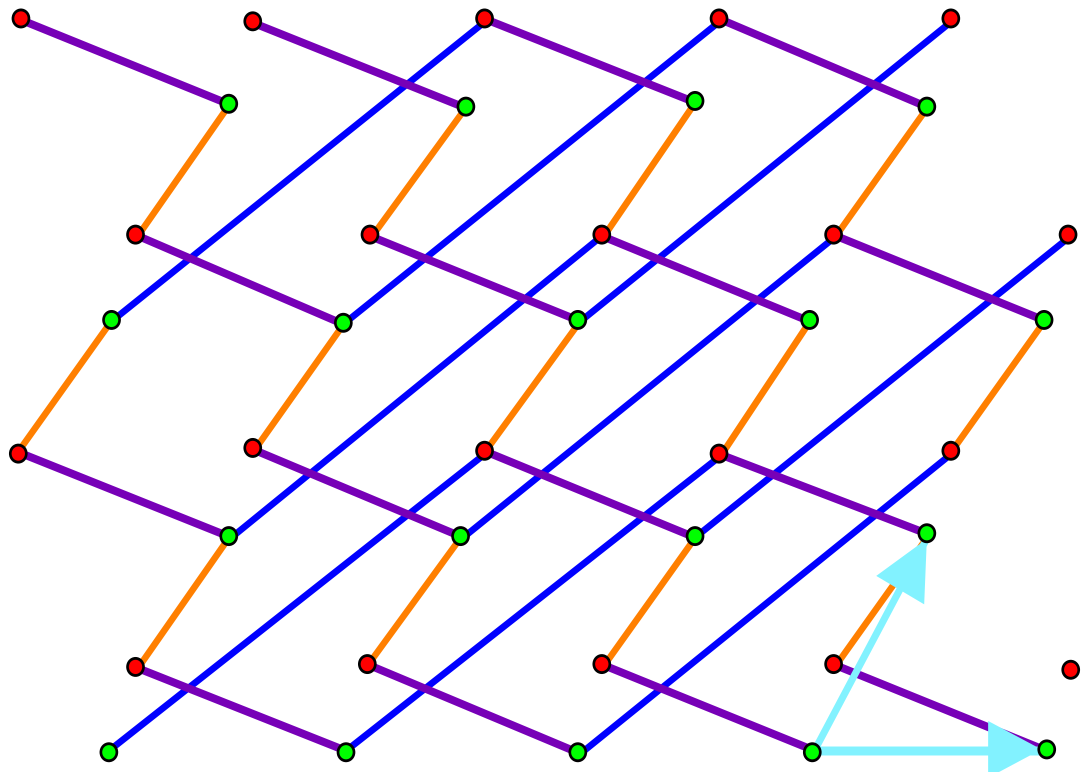
A d-periodic graph is a pair (G, Γ), where G = (V, E) is a simple infinite graph with vertices V , edges E and finite degree at every vertex, while $\Gamma \subset Aut(G)$ is a free Abelian group of automorphisms that has rank d, acts without fixed points and has a finite number of vertex (and hence, also edge) orbits.

A periodic placement of a d-periodic graph (G, Γ) in R^d is defined by two functions:

$$p: V \rightarrow R^d \quad \text{and} \quad \pi: \Gamma \rightarrow T(R^d)$$

with p assigning points in R^d to the vertices of G and π a faithful representation of Γ into the group of translations, with image a lattice of rank d.

These two functions must satisfy $p(gv) = \pi(g)(p(v))$



Fragment of a 2-periodic framework (d = 2), with n = 2 equivalence classes of vertices and m = 3 equivalence classes of edges. The generators of the periodicity lattice are marked by arrows, which, in this example, are not edges.

Figure from Borcea, C.S. and Streinu, I.: Minimally rigid periodic graphs, Bulletin LMS (2011) .

Given a periodic placement (G, Γ, p, π) , we may fix the length of all edges

$$\ell(u,v) = |p(v) - p(u)|$$

and obtain a weighted periodic graph (G, Γ, ℓ). Assuming G connected, we also refer to (G, Γ, p, π) as a periodic framework.

A realization of the weighted d-periodic graph (G, Γ, ℓ) in R^d is a periodic placement that induces the given weights.

Realizations that differ by an isometry of R^d will be considered as the same configuration, hence the configuration space of (G, Γ, l) is the quotient space of all realizations by the group $E(d)$ of all isometries of R^d.

The deformation space of a periodic framework (G, Γ, p, π) is the connected component of the corresponding configuration.

For tetrahedral crystal frameworks (e.g. silica and zeolites), the infinitesimal deformation space is at least three-dimensional.

[Borcea-Streinu, Thm. 4.2, pg. 2644]

2. Frameworks of the silica polymorphs: cristobalite, quartz and tridymite

Structural determinations for these silica polymorphs date back to the early days of X-ray diffraction.

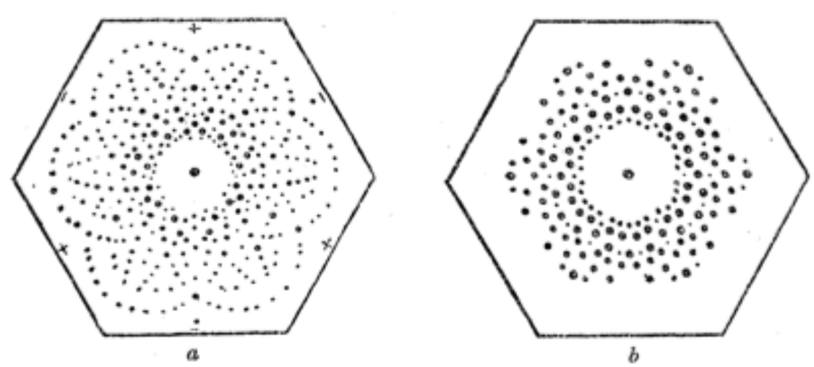
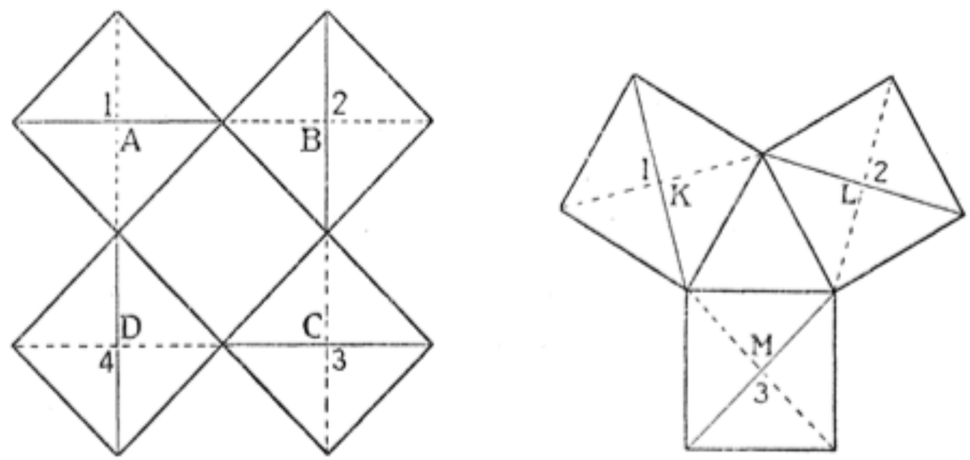


Fig. 7.—*a* and *b*. Laue diagrams of α quartz and β quartz. After F. Rinne.

Figure from Bragg, W.L. and Gibbs, R.E.: The structure of α and β quartz, Proc. Roy. Soc. A 109 (1925), 405-427.

The framework structures of quartz, cristobalite and tridymite can be described as periodic articulations of tetrahedra with oxygen at the vertices and silicon at the center of each tetrahedron.



Structural diagrams for high cristobalite and high quartz (projections); from Gibbs, R.E.: The polymorphism of silicon dioxide and the structure of tridymite, Proc. Roy. Soc. A 113 (1926), 351-368.

An illustration with ``kissing spheres” for the local disposition of oxygen.

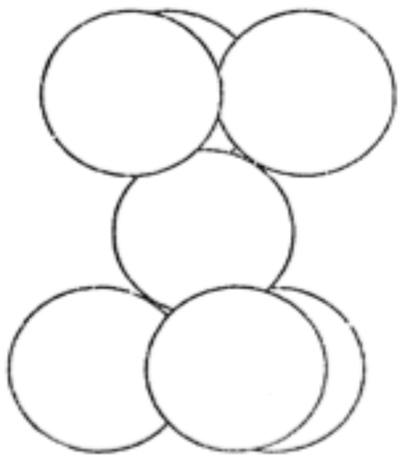


Fig. 12.—Cristobalite.

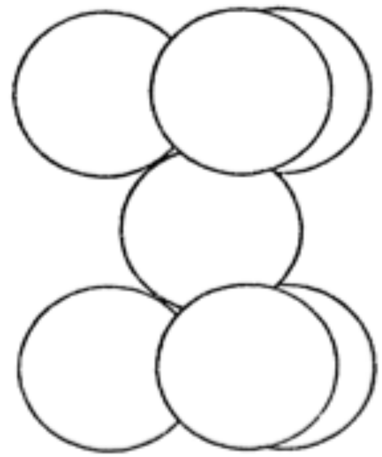


Fig. 13.—Tridymite.

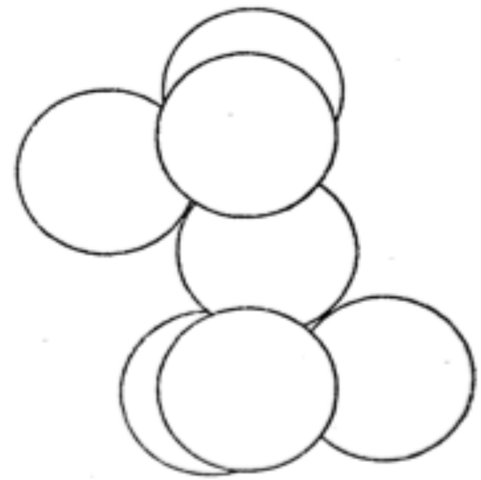
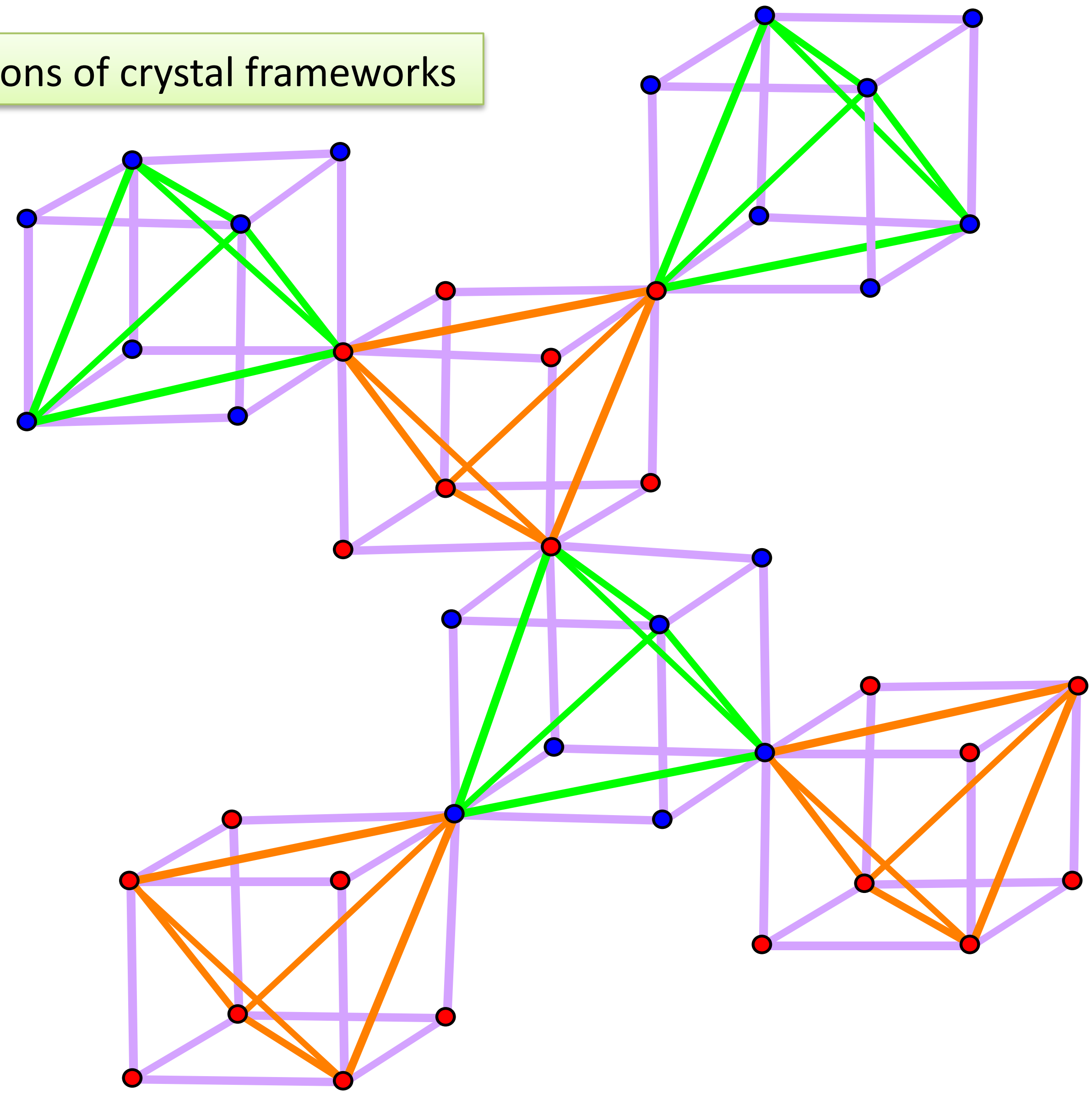


Fig. 14.—Quartz.

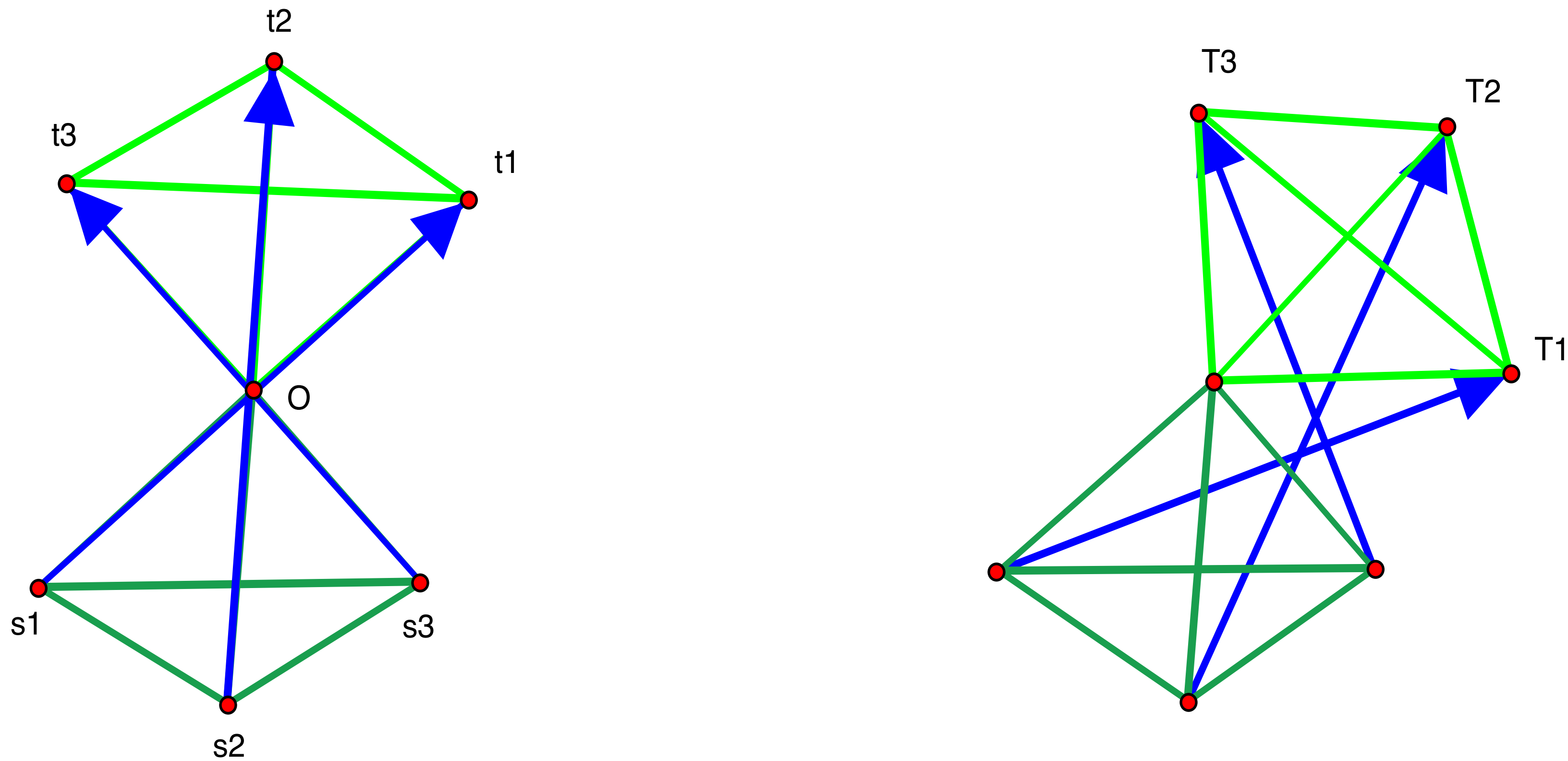
Ibid. Gibbs (1926).

3. Geometric deformations of crystal frameworks

3.1 Cristobalite



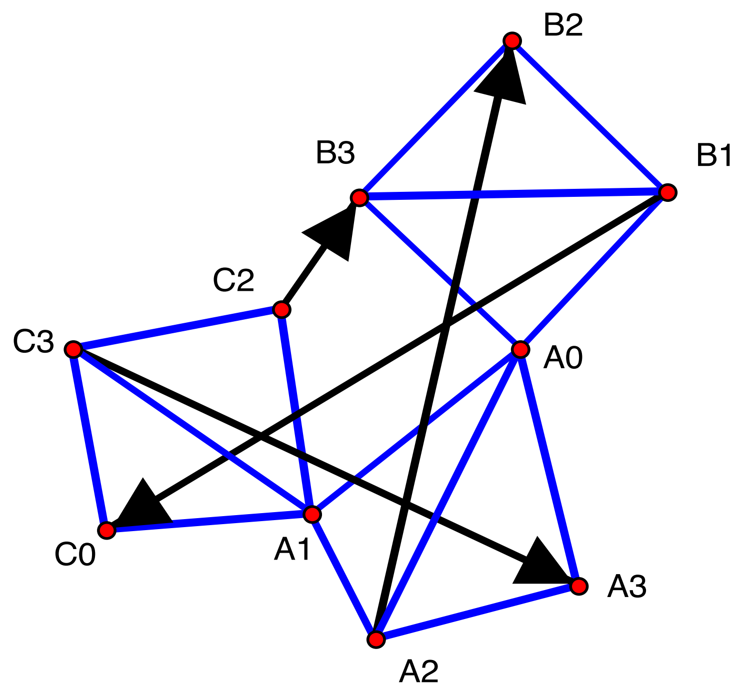
Ideal high cristobalite framework. Cubes are traced only for suggestive purposes.



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

Theorem 1. The deformation space of the ideal high cristobalite framework is naturally parametrized by the open neighborhood of the identity in SO(3) where the depicted generators remain linearly independent.

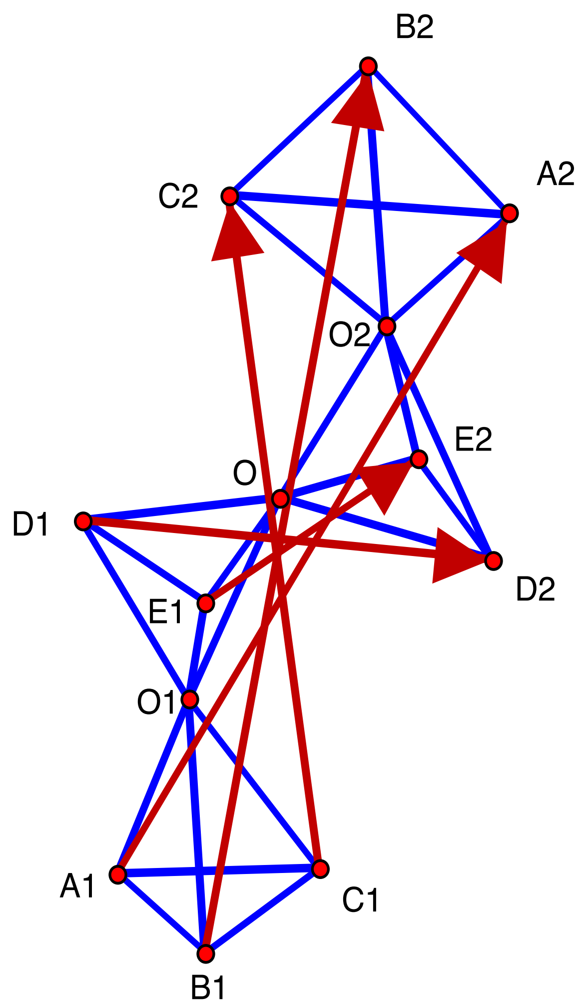
3.2 Quartz



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.

Theorem 2. The deformation space of the quartz framework is naturally parametrized by an open set of the three-dimensional torus $(S^1)^3$.

3.3 Tridymite



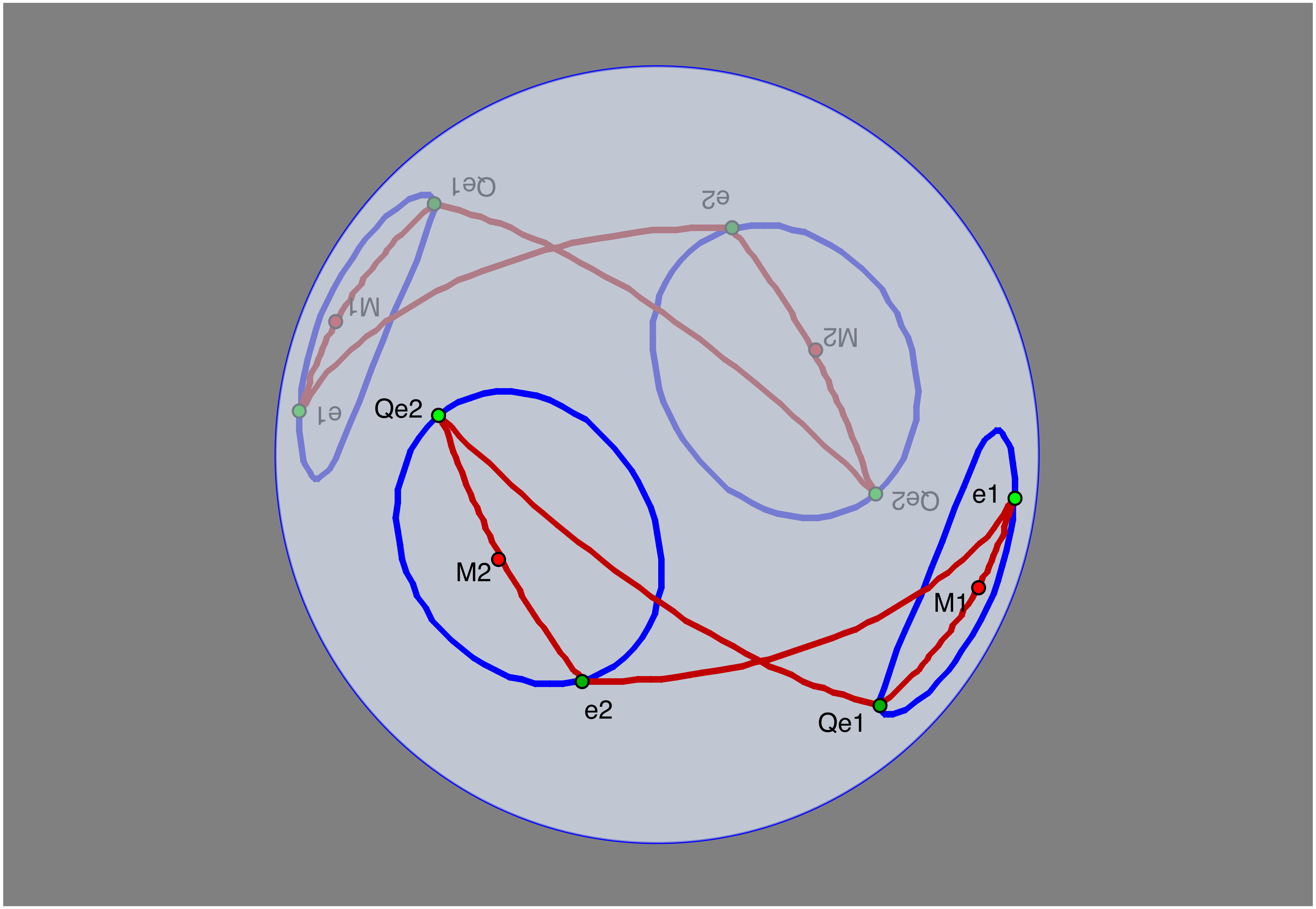
The tetrahedral framework of tridymite. The periodicity lattice is generated by the marked vectors, subject to the relations (C2−C1)+(D2−D1) = (A2 − A1) and (C2 − C1) + (E2 − E1) = (B2 − B1).

With an adequate choice of orthogonal transformations Q, Q_1, Q_2 , maintaining the two relations of linear dependence between the five generators of the period lattice amounts to solving the system

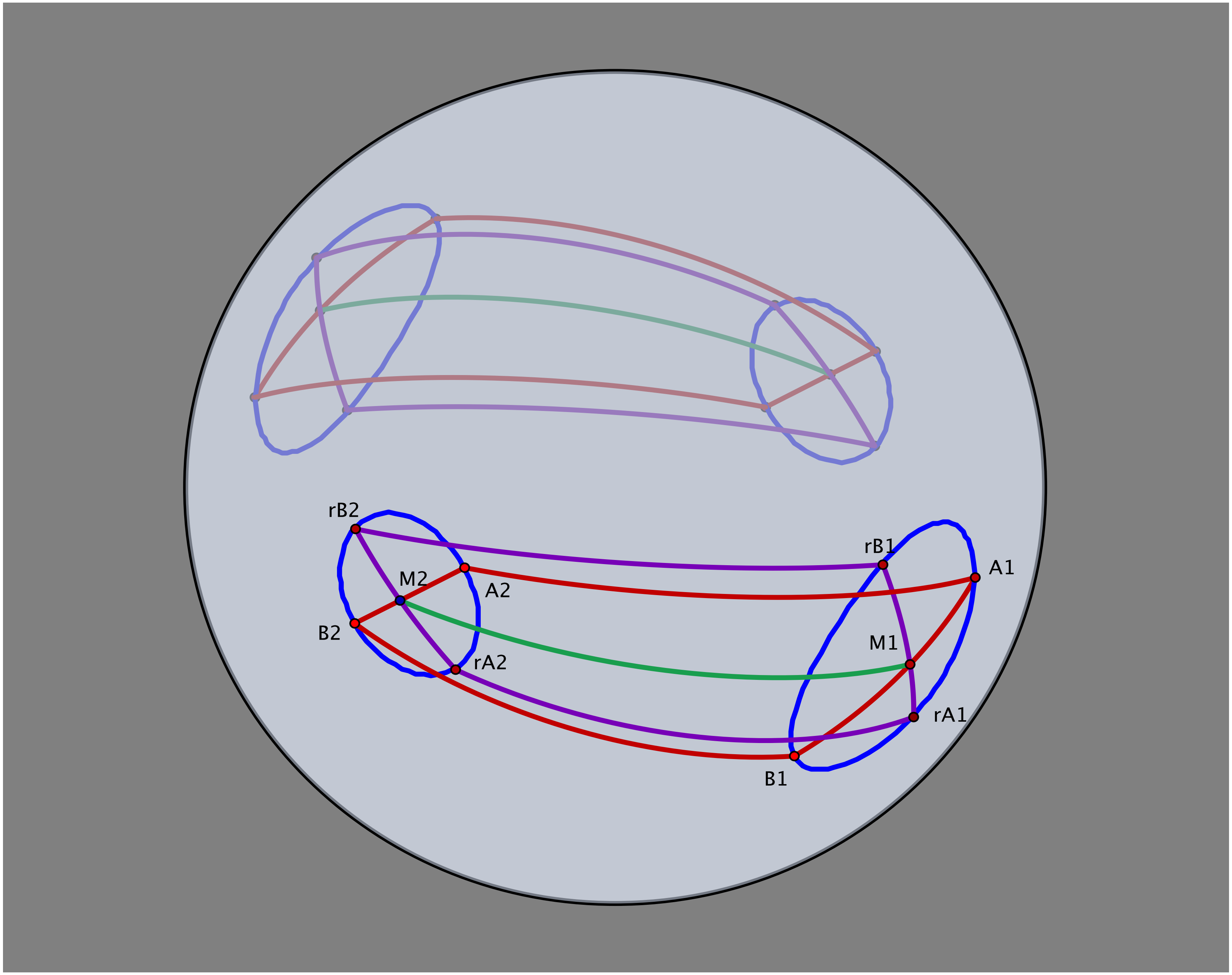
$$e_i + Q\, e_i = Q_1 e_i + Q_2 e_i \qquad i = 1,2$$

Note that Q_i are orthogonal matrices and hence the above system involves quadratic conditions.

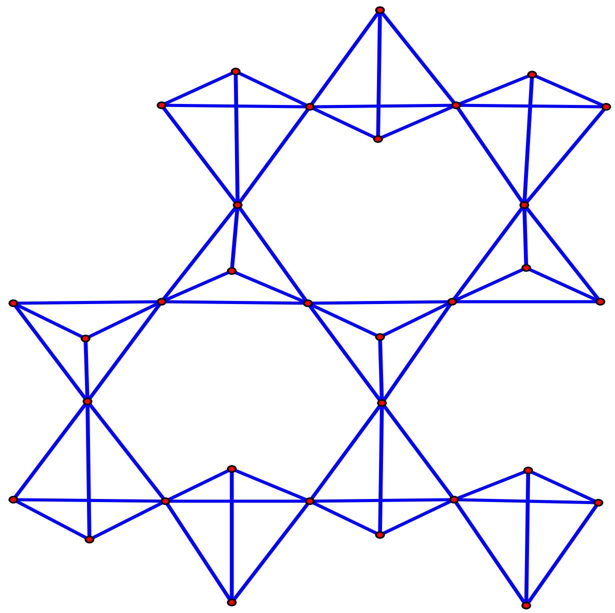
However, we may interpret the system as a problem about a spherical four-bar mechanism and obtain a simple geometrical solution. We assume $Q \in SO(3)$ given in a neighborhood of the identity and we look for solutions Q_1, Q_2.



The spherical four-bar mechanism associated to the system. The geodesic arcs e_1e_2 and Qe_1Qe_2 have length $\pi/2$.



Spherical four-bar mechanism and reflection in [M1,M2].



Fragment of the
ideal high tridymite (the aristotype)

Theorem 3. The deformation space of the tridymite framework in a neighborhood of the aristotype 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 singularity at the aristotype framework.

The tangent space at this singularity is six-dimensional.
Sheets paired by the relabeling involution $(Q_1,Q_2) \rightarrow (Q_2,Q_1)$ meet transversely at the singularity. Otherwise, the ramification locus is of codimension two and is determined by reflection invariant configurations of the spherical quadrilateral.

Summary of results

For a periodic graph (G, Γ), with $G = (V, E)$, we let $|V/\Gamma| = n$ and $|E/\Gamma| = m$.

We have investigated the deformation spaces of the of the ideal framework structures associated to three silica polymorphs (cristobalite, quartz and tridymite) for the maximal periodicity lattice of the high phase.

For cristobalite (n=4,m=12) and quartz (n=6,m=18), the deformation spaces are smooth three-dimensional manifolds.

For tridymite (n=8,m=24), the deformation space is singular and can be described in a neighborhood of the aristotype as a ramified covering with four-sheets of a three-dimensional domain.

Selected references from crystallography and mineralogy:

[BG] Bragg, W.L. and Gibbs, R.E.: The structure of α and β quartz, Proc. Roy. Soc. A 109 (1925), 405-427.

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[G2] Gibbs, R.E.: The polymorphism of silicon dioxide and the structure of tridymite, Proc. Roy. Soc. A 113 (1926), 351-368.

[GD] Grimm, H. and Dorner, B.: On the mechanism of the a-b phase transformation of quartz, J. Phys. Chem. Solids 36 (1975), 407-413.

[P1] Pauling, L.: The structure of some sodium and calcium aluminosilicates, Proc. Nat. Acad. Sci. 16, no.7 (1930), 453-459.

[P2] Pauling, L.: The structure of sodalite and helvite, Z. Kristallogr. 74(1930), 213-225.