Potential solutions to mathematical challenges for solid crystalline materials

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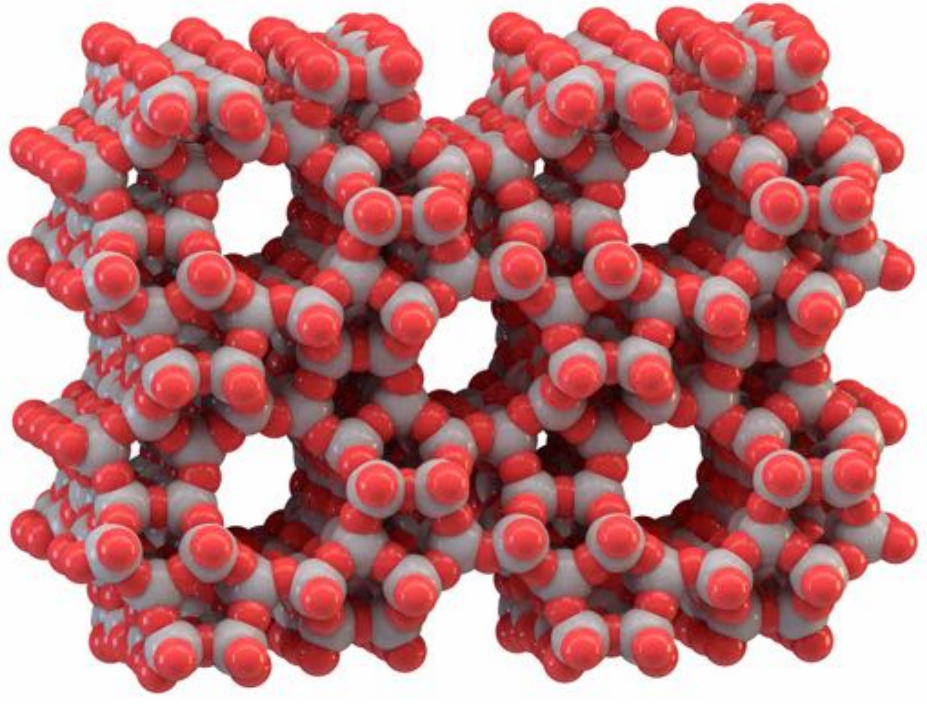
Crystals are periodic frameworks

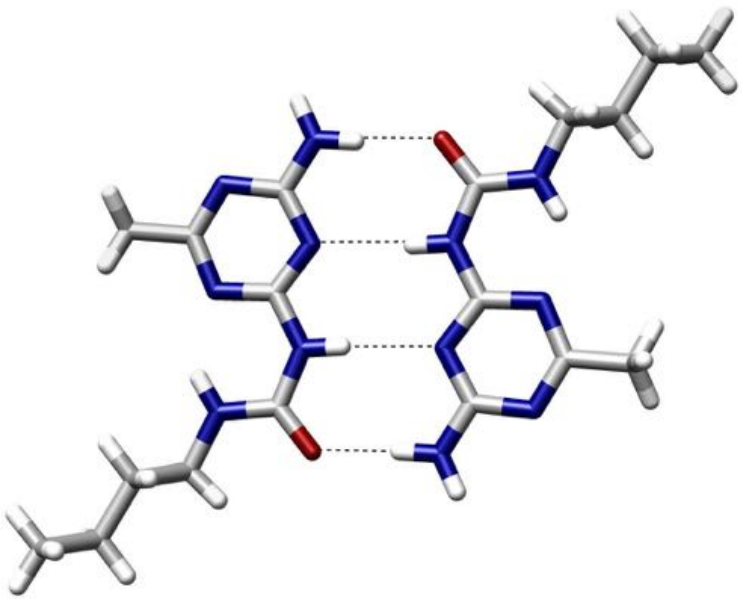
An ideal crystal is a periodic framework (an infinite graph in $\mathbb{R}^3$) of repeated patterns of atoms or molecules that form a solid body.

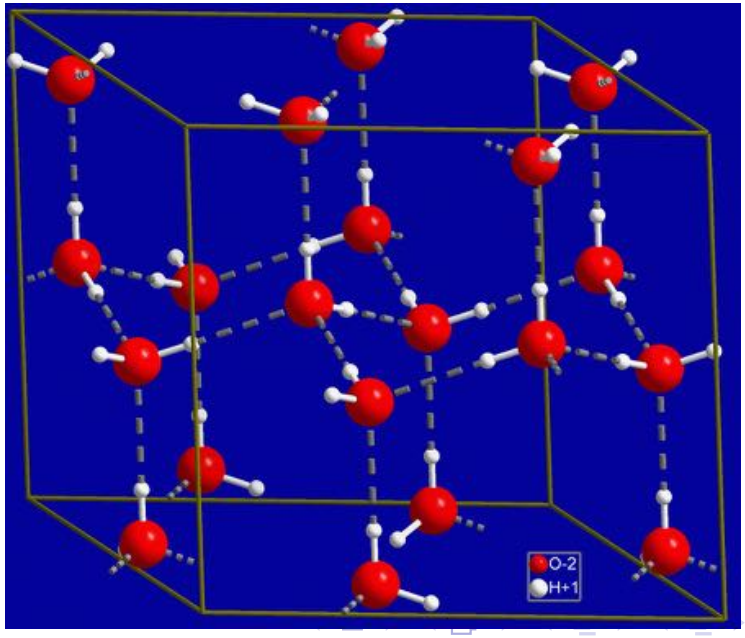


Zeolites above can adsorb liquid and gases..

A metal-organic framework

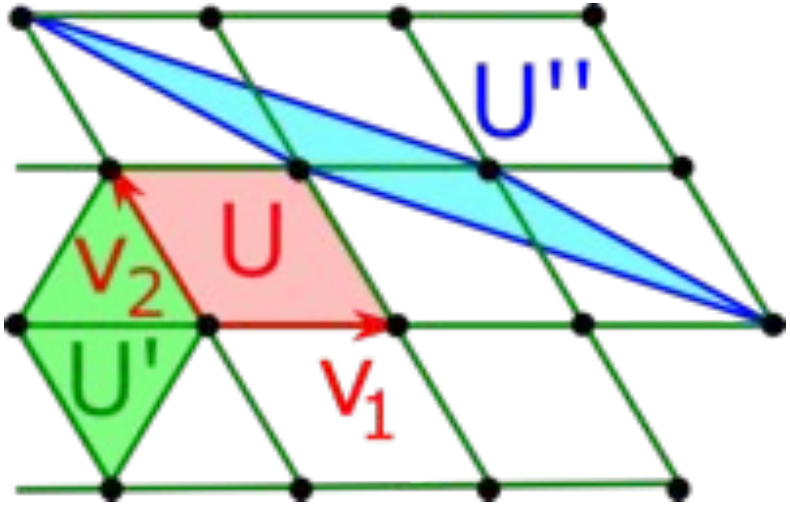
is a collection of molecules containing organic and metal atoms. Chemical bonds within a molecule are strong, bonds between atoms from different molecules are weaker, but sufficiently many of them can make the crystal rigid.





Any crystal has a lattice

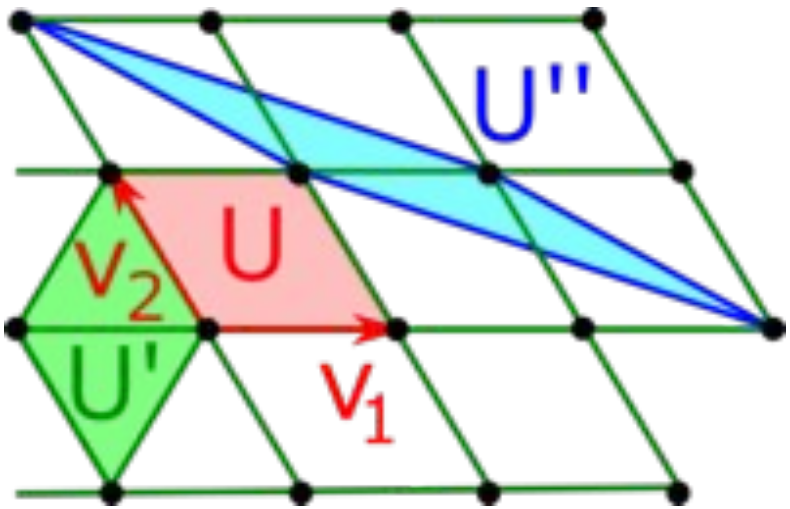
Definition. Let vectors $\vec{v}_1, \ldots, \vec{v}_d$ form a basis, i.e. any vector in $\mathbb{R}^d$ can be uniquely expressed as $\sum_{i=1}^{d} t_i \vec{v}_i$ with $t_i \in \mathbb{R}$. If all t_i are integer, the discrete set of points $\{\sum_{i=1}^{d} t_i \vec{v}_i\}$ is a *lattice* $L \subset \mathbb{R}^d$.



The vectors $\vec{v}_1 = (1, 0)$, $\vec{v}_2 = (0, 1)$ define a square lattice in $\mathbb{R}^d$, see the triangular lattice on the left.

Any lattice has many unit cells

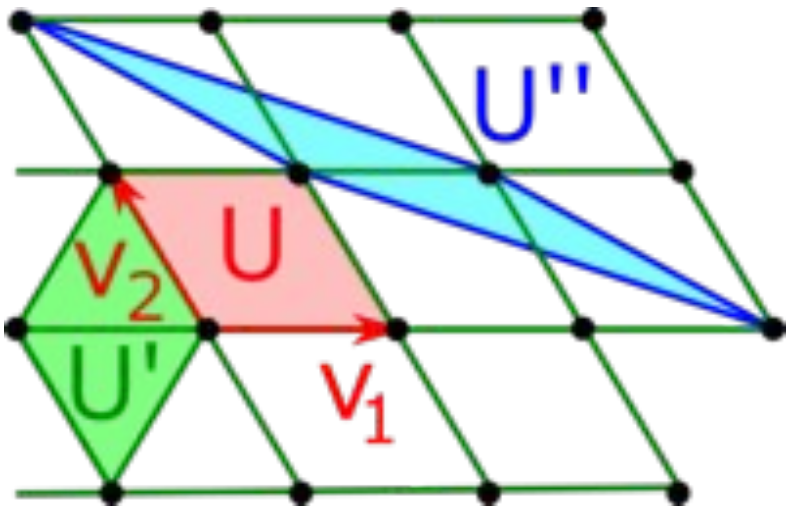
If t_i are real and restricted to the interval $[0, 1]$, $U = \{\sum_{i=1}^{d} t_i \vec{v}_i\} \subset \mathbb{R}^d$ is a *unit cell* of the lattice L, a non-rectangular box with parallel opposite sides.



The cells U, U', U'' (and infinitely many others) define the same lattice, so unit cells are ambiguous.

A lattice representation

The aim is to represent any lattice (later any crystal) in a unique way, otherwise any algorithm comparing lattices (or crystals)



can be confused because very different inputs can represent the same (or nearly equivalent) lattices.

The aim is to improve the data representation.

An equivalence of lattices

Definition. Lattices are called *equivalent* if they can be related by a rigid motion of $\mathbb{R}^d$ (for $d = 3$, a composition of rotations and translations).

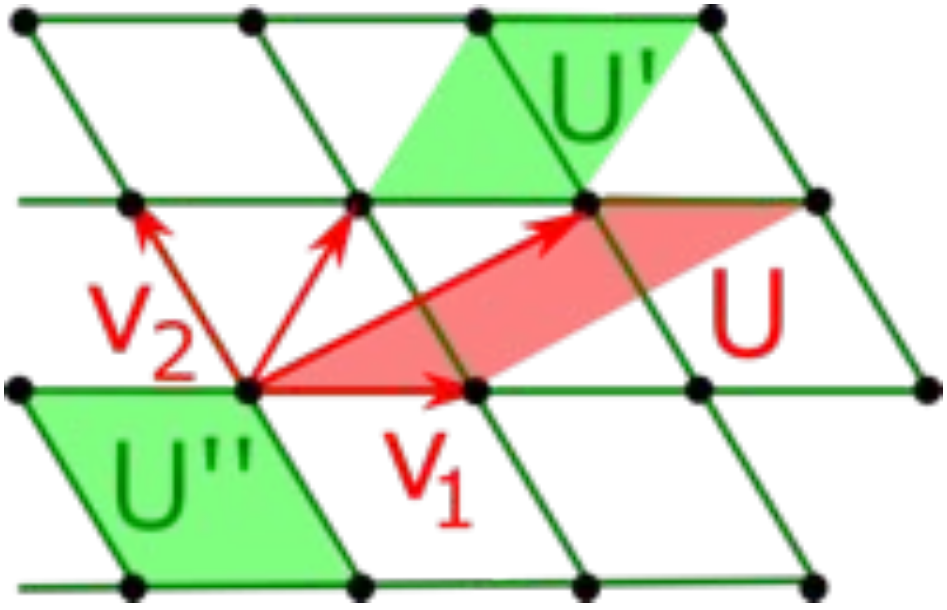
Motivation : solid crystals are rigid bodies.

Classification problem. Determine if two lattices (given by their unit cells) equivalent?

A natural attempt is to find a unique unit cell for any lattice, i.e. compare lattices via unique cells.

Niggli's reduced cell

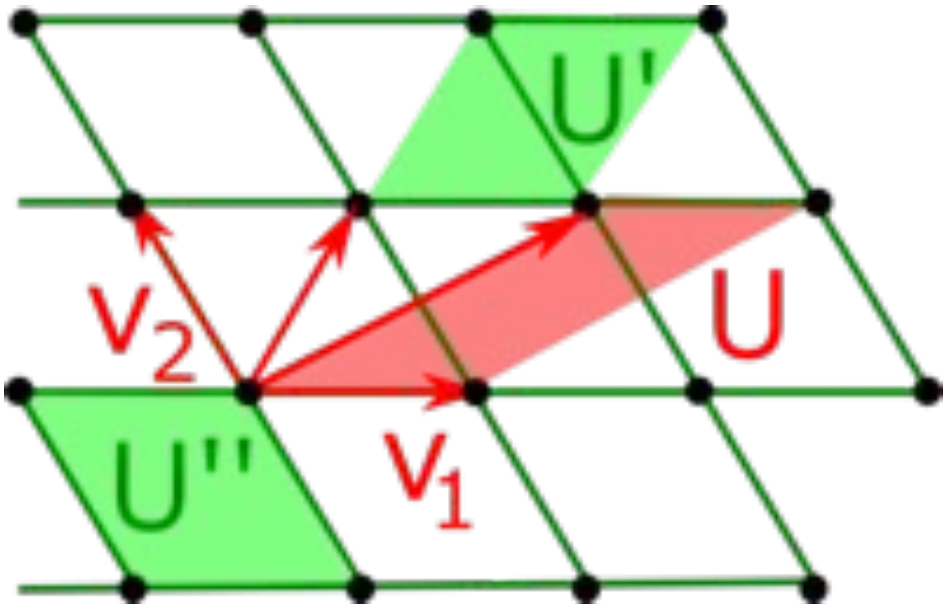
is the best of known reduced cells, because it is 'unique' (first published in 1928 in German).



If the orthogonal projection of $\vec{v}_2$ to the line of $\vec{v}_1$, is outside $[-0.5|\vec{v}_1|, 0.5|\vec{v}_1|]$, add multiples of $\vec{v}_1$ to make the vector $\vec{v}_2$ shorter.

A non-reduced cell U is reduced to U' or U''.

Niggli's reduction choices



One can exclude one of the projected end-points $\pm 0.5|\vec{v}_1|$, but this choice cuts the continuous space of all possible lattices.

Any choice makes close lattices distant similarly to choosing an initial meridian for measuring longitudes on Earth. Why is this not enough?

A yes/no answer for lattices

To compare lattices (similarly crystals) given by unit cells, we can first obtain Niggli's reduced cells and then compare their parameters.

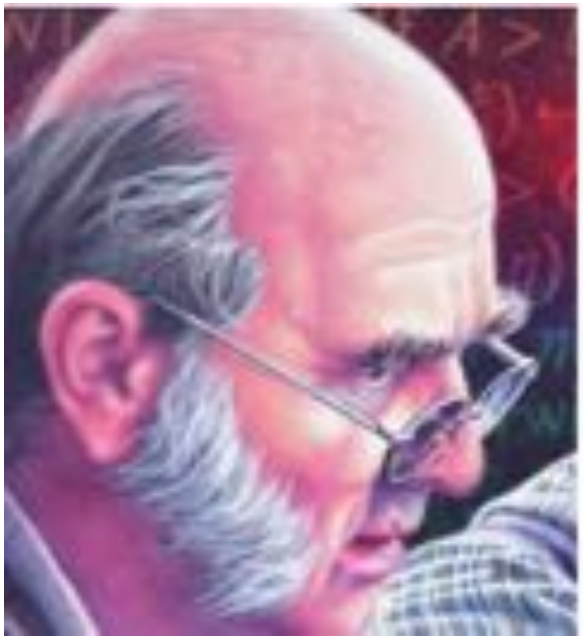
An answer is yes (equivalent lattices) or no.

All real data are noisy and most lattices (similarly crystals) are different in practice.

What happens if a lattice is slightly perturbed?

Niggli's reduced cell is unstable

If a lattice is perturbed, its Niggli's reduced cell can substantially differ from the reduced cell of the original lattice [L. Andrews et al. 1980]. Hence a similarity between lattices is lost.



My main interest for several decades has been to find a measure of the difference between pairs of lattices. Surprisingly, this is not a mathematical problem with a well-defined solution. With my colleague, I have published several articles, each improving on the previous methods. Two important uses for our work are the identification of the crystal class of a crystal and the creation of databases based on crystal metrics.

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How different are two lattices?

All lattices form a continuous space, because any lattice can be continuously deformed into another. This continuous space is traditionally split into disjoint subspaces: cubic, triclinic etc (called crystal systems or Bravais lattices).

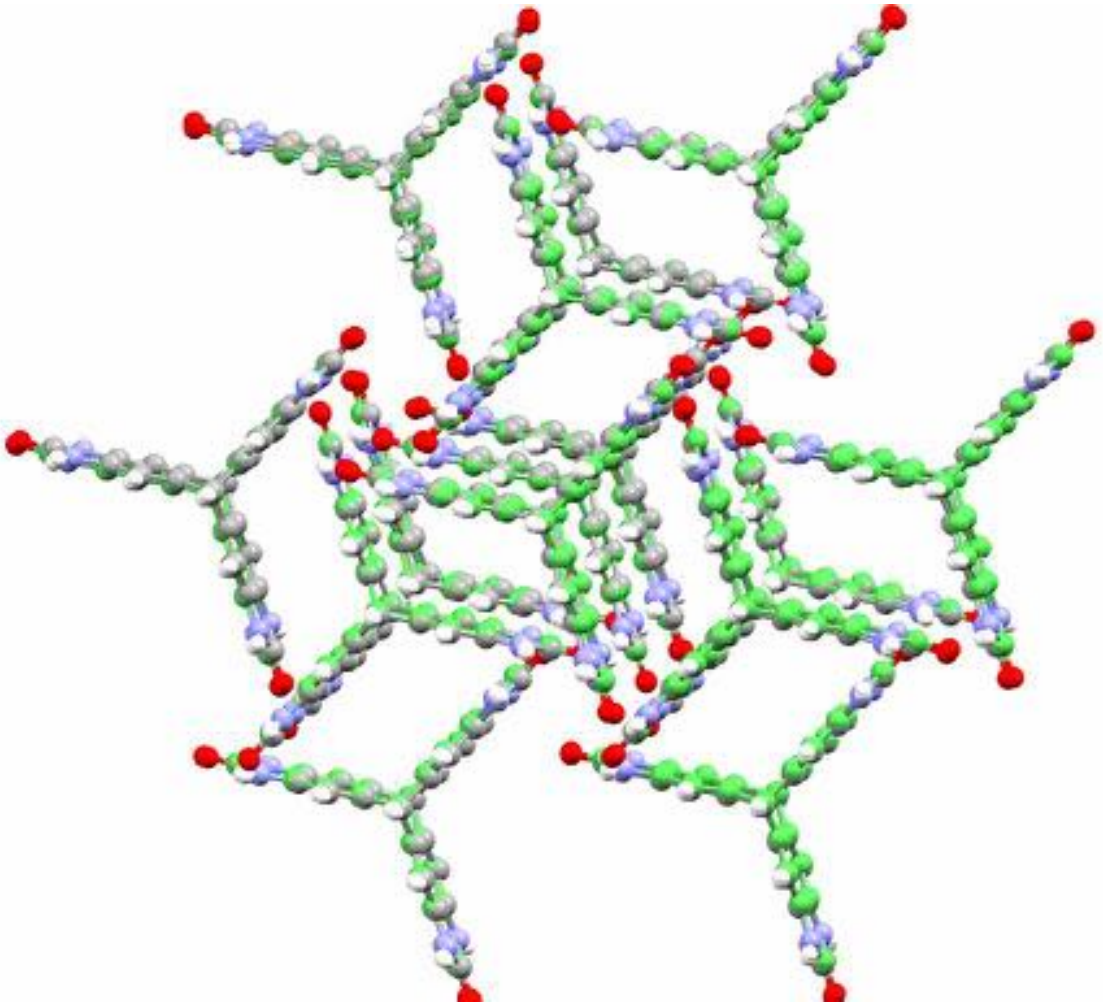
Any such discrete classification, e.g. by using symmetry groups, cannot quantify a similarity between all lattices (hence crystals).

Currently available distances

Given two crystals, Mercury tries to match a number of molecules (15 by default) in both crystals by finding a best rigid motion, and outputs the root-mean-square deviation $\sqrt{\frac{1}{n}\sum_{i=1}^{n}||p_i - q_i||^2}$ between n matched atoms.

If the partial match is extended to infinite crystals, this root-mean-square deviation infinitely grows and becomes meaningless.

A partial match of molecules



Two crystals overlaid:

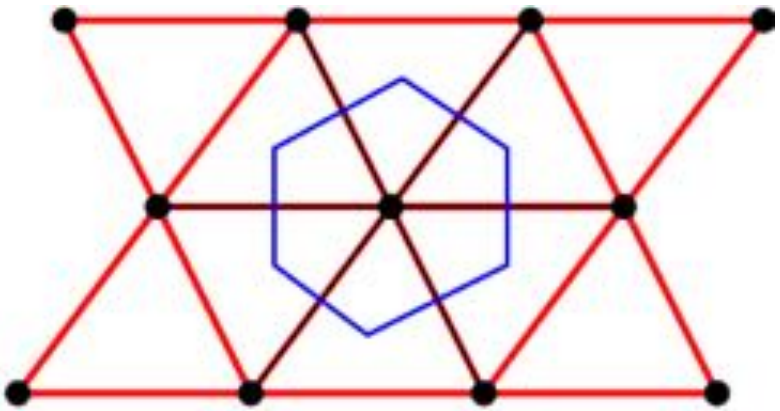
Root Mean Square distance between atoms is 0.17A.

What if we match 30 molecules?

The Voronoi cell of a lattice L

For a fixed point $p \in L$, the *Voronoi cell* is the neighbourhood of points $q \in \mathbb{R}^d$ that are closer to p than to all other points of the lattice L:

$$V(L) = \{q \in \mathbb{R}^d \,:\, d(q,p) \leq d(q,s),\ s \in L - p\}.$$

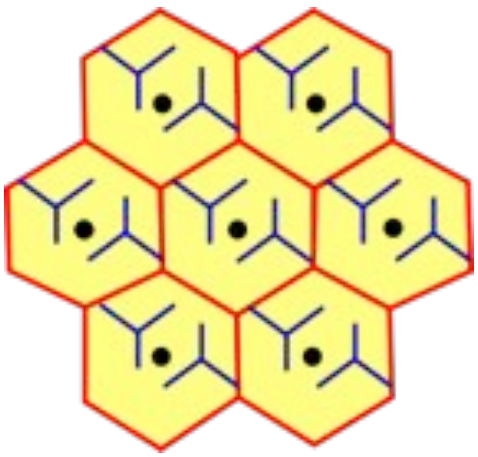


The boundary of the Voronoi cell centered at $0 \in \mathbb{R}^2$ is blue.

For $d = 2$, the Voronoi cell $V(L)$ is a rectangle or (generically) a centrally symmetric hexagon.

The Voronoi cell generates a lattice

Similarly to a traditional unit cell, the Voronoi cell doesn't depend on a point $p \in L$ and tiles $\mathbb{R}^d$.



Any crystal can be represented by a set of atoms or molecules in its Voronoi cell $V(L)$, which is unique up to translations and rotations (isometries of $\mathbb{R}^d$).

The combinatorial structure of a Voronoi cell may change (from a hexagon to a rectangle), so they are easier to compare geometrically.

Axioms for a metric or a distance

For any objects (cells, crystals) S, S', a metric $d(S, S')$ should satisfy non-degenerate positivity $d \geq 0$, symmetry $d(S, S') = d(S', S)$, triangle inequality $d(S, S') + d(S', S'') \geq d(S, S'')$.

Many attempts to define a distance between crystals fail the non-degeneracy saying that $d(S, S') = 0$ *only if* S, S' are equivalent.

When do metric axioms fail?

A typical attempt represents a crystal by a vector of numerical features and then takes a Euclidean (or another) distance on vectors.

When different crystals have the same features, the distance between the identical vectors is 0, which violates the non-degeneracy condition.

We need to avoid trivial examples: $d(S, S') = 1$ for any different crystals. Hence a range of possible distances should be continuous.

How are Voronoi cells computed?

CGAL finds Voronoi cells only for cubic lattices.

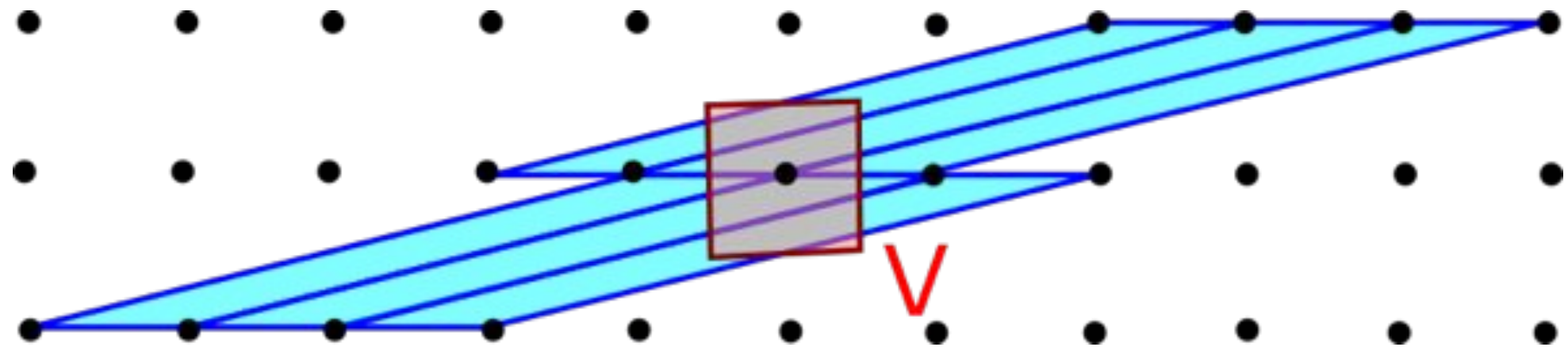
Zeo++ finds Voronoi cells for any lattice $L \subset \mathbb{R}^3$ as follows: the Voronoi cell of any point $p \in U$ is found by considering only points of L within the $3 \times 3 \times 3$ extension of any given unit cell U.

Unfortunately, no fixed extension is enough if a unit cell is arbitrary, so Zeo++ fails sometimes.

Why may cell extensions not help?

Claim. For any integer $k > 1$, there is a unit cell U (parallelepiped in $\mathbb{R}^d$) whose k-fold extension doesn't cover the Voronoi cell of the lattice of U.

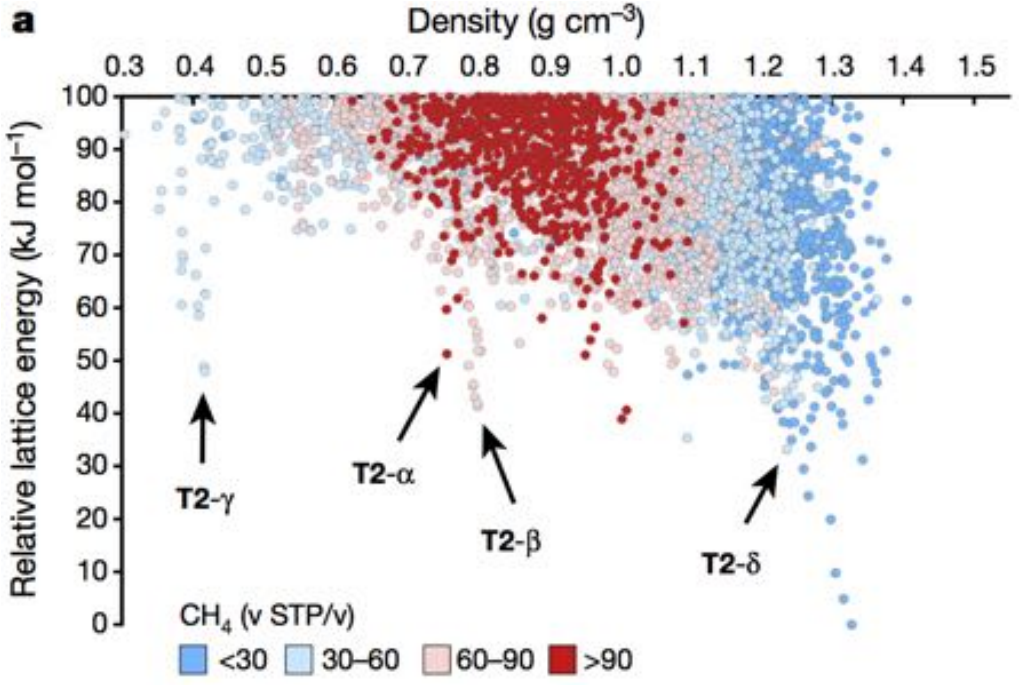
Proof outline in $\mathbb{R}^2$: the 4-fold extension of U doesn't cover the square Voronoi cell below.

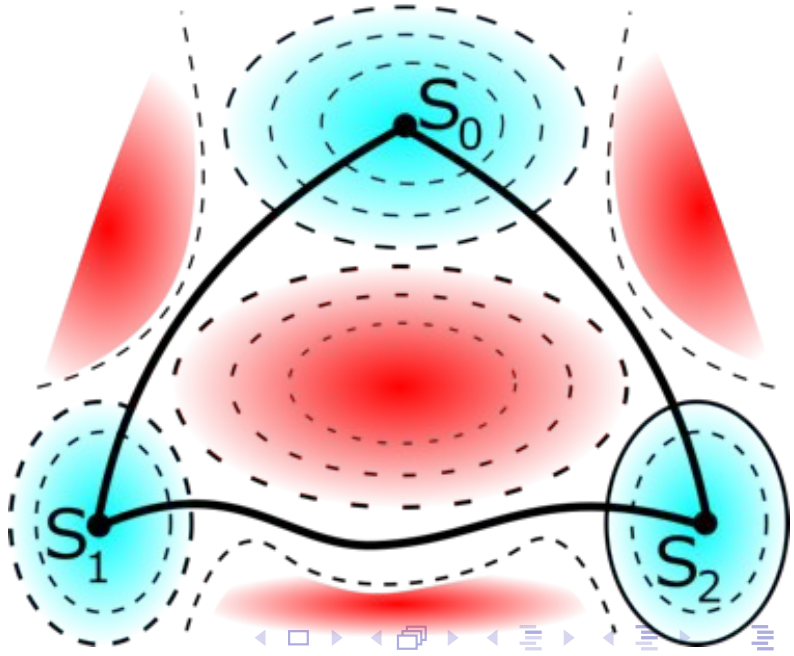


Benefits of space continuity

Left: state-of-the-art from the 2017 Nature paper by Angeles Pulido,. . . , Graeme Day.

Right: dream map of all polymorphs shows continuous transitions paths between minima.





Summary of challenges/solutions

Crystals form a continuous space, hence should be classified by continuous invariants (stable under perturbations). The Voronoi cell reduces the classification up to isometries to a finite set.

Continuous invariants will map the space of all potential crystals and show which polymorphs are *structurally close* in this continuous space.

Many thanks to collaborators: Graeme Day, Angeles Pulido, postdoc Ana Garcia, PhD students Phil Smith, Marco Mosca, Milo Torda.