Introduction to Periodic Geometry for materials applications

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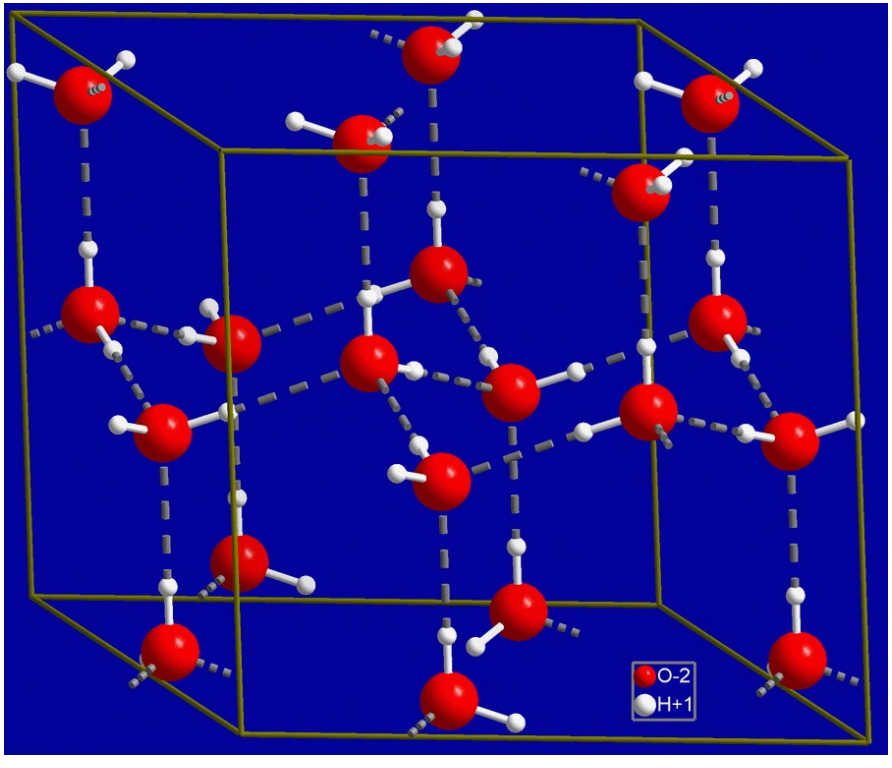
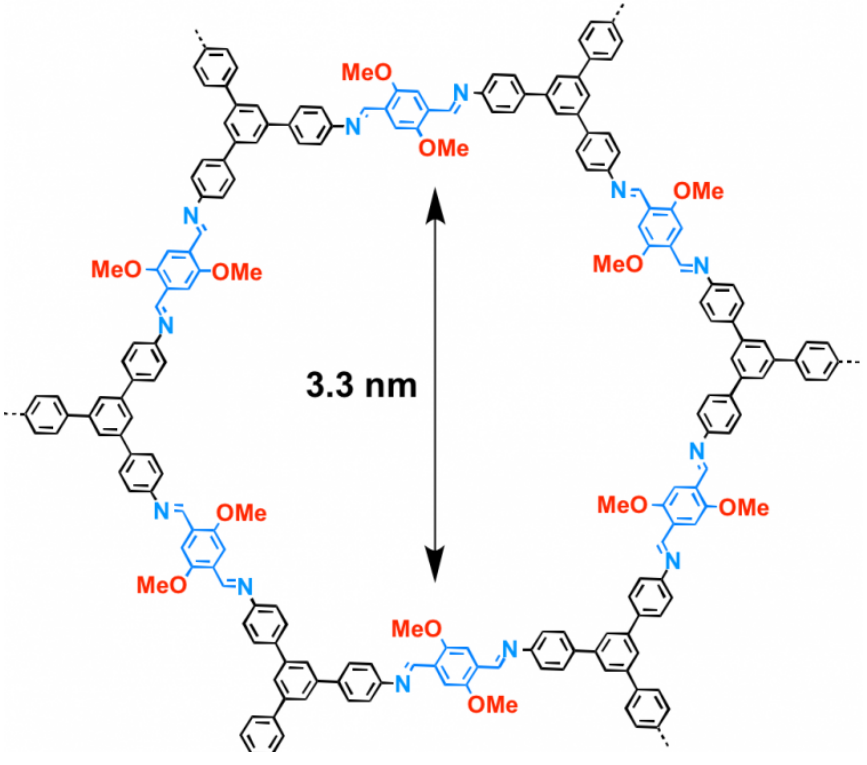
Objects : all periodic crystals

Solid crystalline materials (periodic *crystals*) can have many types, all consist of elementary blocks (*motifs*) of atoms, ions or molecules in a *unit cell* periodically repeated in three directions.





Past: crystal = (unit cell, motif)

A crystal is usually given by a Crystallographic Information File (CIF) with parameters of a unit cell, types and fractional coordinates of atoms.

A *unit cell* $U = \{x\vec{v}_1 + y\vec{v}_2 + z\vec{v}_3 \mid x, y, z \in [0, 1)\}$ is a parallelepiped spanned by a basis $\vec{v}_1, \vec{v}_2, \vec{v}_3$.

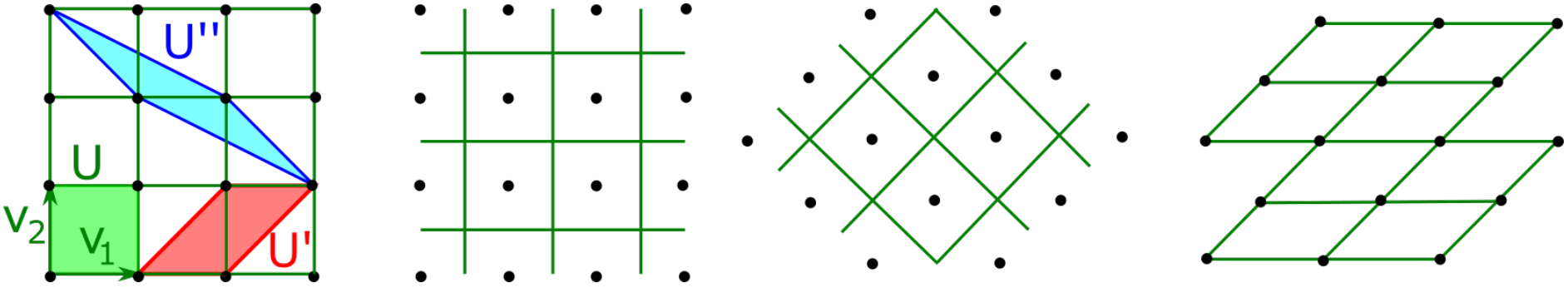
A *motif* is a finite set of points with chemical types and coordinates x, y, z in the cell basis.

We model a crystal as a *periodic set of points*.

Extra properties or bonds can be easily added.

Ambiguity for lattices and crystals

A *lattice* is a periodic set with a 1-point motif.



Are these four lattices equivalent or different?

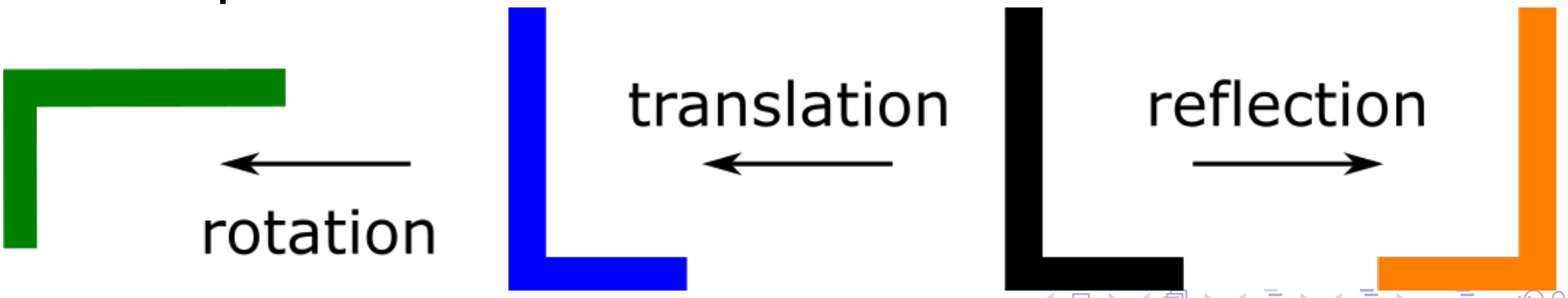
All highlighted unit cells (called *primitive*) have a minimal volume. Any crystal can be represented by *infinitely many* pairs (a unit cell, a motif).

What crystals should be considered *equivalent*?

Crystals up to isometries

Crystal structures are determined in a **rigid** form, so should be studied up to *rigid motions*.

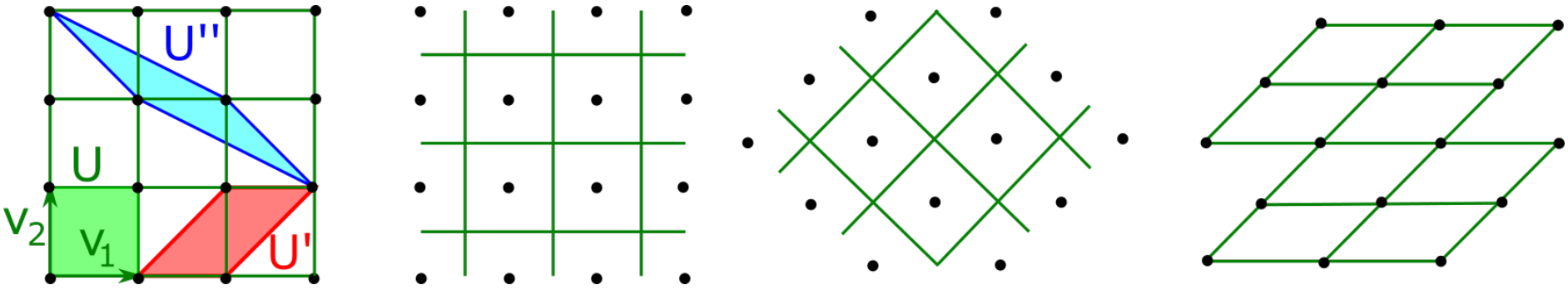
An *isometry* of $\mathbb{R}^n$ is any map that preserves all distances between points. A *rigid motion* also preserves an orientation of $\mathbb{R}^n$, e.g. a reflection is not a rigid motion. Rigid motions in $\mathbb{R}^3$ are compositions of translations and rotations.



What is a crystal finally?

So a crystal is not a single set of points (CIF).

Crystal $=$ **isometry class** of infinitely many periodic point sets up to rigid motion in $\mathbb{R}^n$.



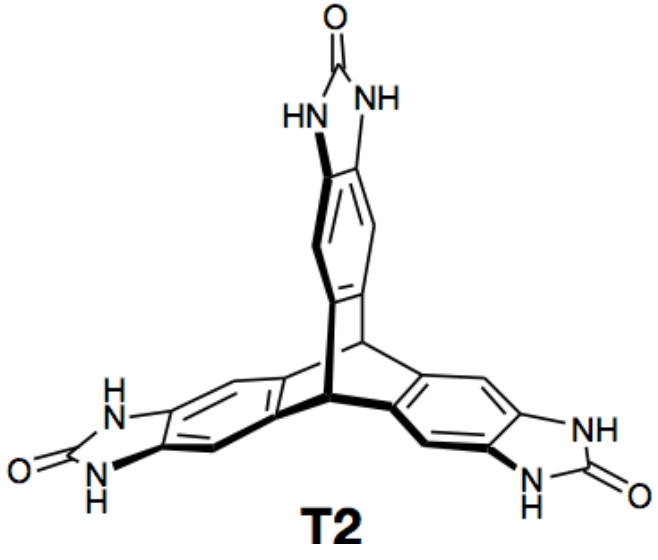
These four lattices and infinitely many others form a *single isometry class* of square lattices.

CSP: Crystal Structure Prediction

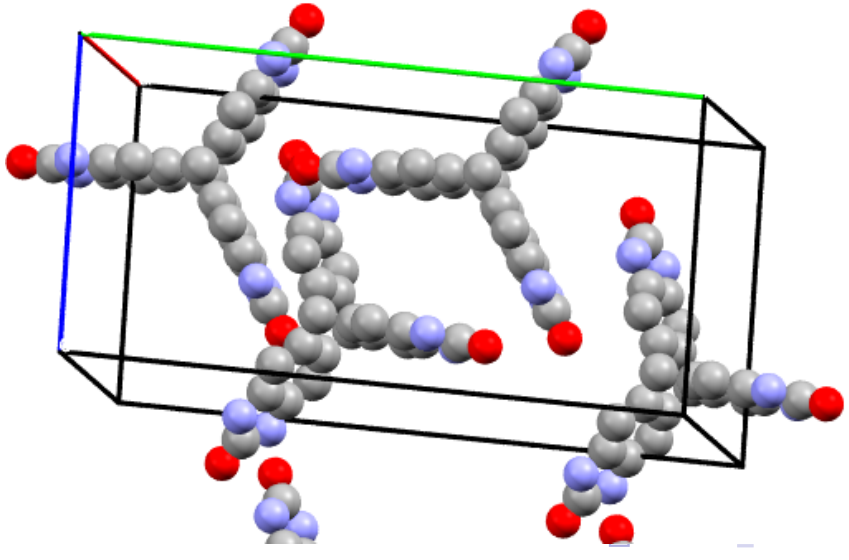
Aim : discover crystals with target properties,

predict *stable* crystals obtained by embedding several molecules or atoms into a unit cell.

The stability is determined by an *energy*, which depends on atomic positions and charges.

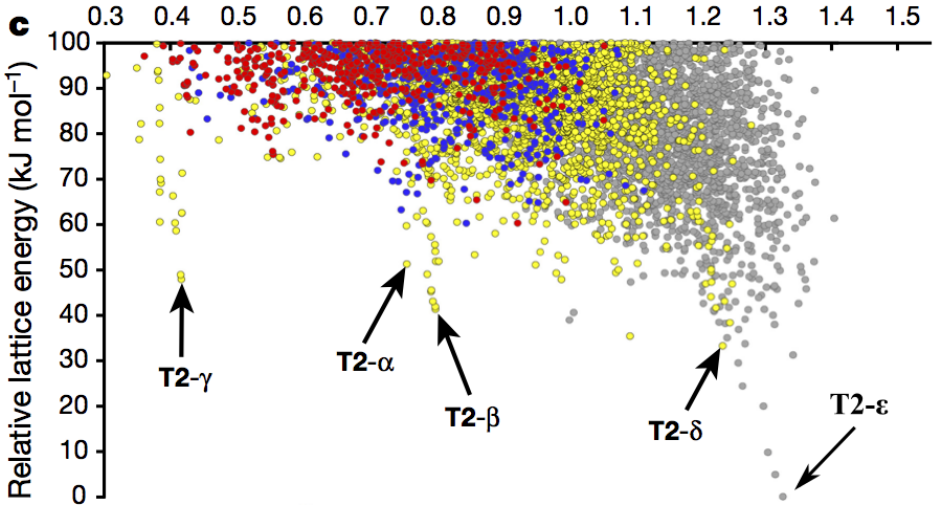


T2



Embarrassment of over-prediction

coined by Prof Sally Price FRS (UCL) says that the state-of-the-art CSP software outputs too many approximate local minima of the energy: random start, perturb atoms, compute again, ...

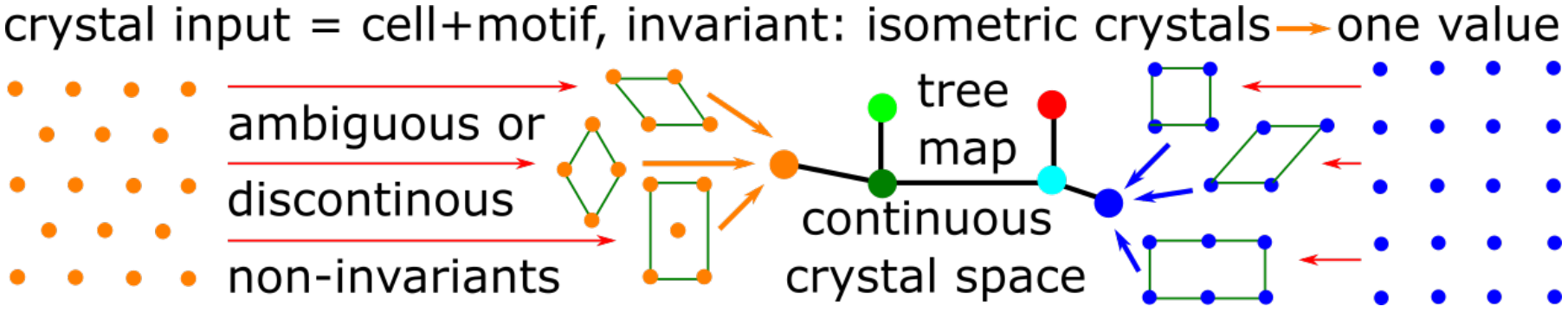


The plot in Nature 2017 shows 5679 predicted crystals of T2 molecules, only 5 were synthesised.

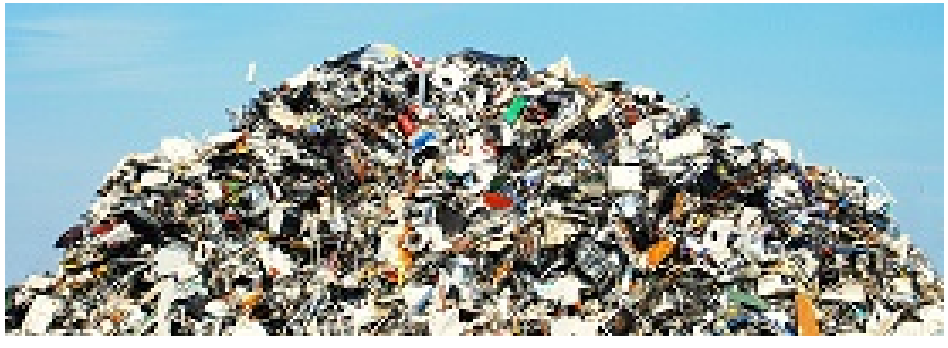
Each crystal is represented by (density, energy). Resources are wasted on many near duplicates.

Isometry invariants of crystals

Invariants (numbers, vectors, matrices,...) must take the *same value* for all isometric crystals.



If a **non-invariant** takes two different values on two crystals, then no conclusion can be made.

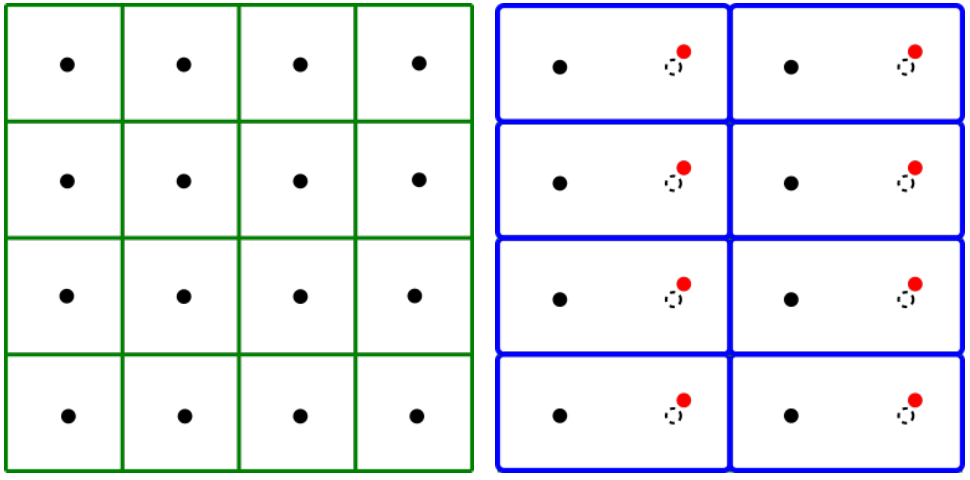


Question: how about non-invariant *big* data?

Answer: use invariants.

Do we have enough invariants?

Crystallography has known the 230 symmetry groups of 3D crystals since 19th century. They are invariants, but are not enough to classify 1M+ crystals in the CSD. The disadvantage of discrete invariants is discontinuity under noise.



Under a small perturbation, a primitive cell is doubled, so its volume is discontinuous.

Isometry classification problem

We need a complete and continuous isometry *invariant* of crystals $I : \{\text{crystals}\} \to \{\text{numbers}\}$

1) *invariance* : if any crystals S, Q are isometric, then $I(S) = I(Q)$, i.e. I should be well-defined on isometry classes of crystals with fixed positions.

2) *completeness* : if $I(S) = I(Q)$, then S, Q are isometric, i.e. I distinguishes all crystals $S \neq Q$;

3) *continuity* : the invariant I slightly changes under perturbations to quantify a similarity, else we miss nearly identical crystals at local minima.

More classification requirements

4) *Computability* : a polynomial time in a motif size (the number *m* of atoms in a unit cell).

Past: energy-vs-density plot of 5679 predicted T2 crystals took 12 weeks on a supercomputer.

5) *Reconstructability* : a complete invariant should allow us to reconstruct a full 3D crystal so that we can choose a new invariant value and discover new crystals with extraordinary properties, e.g. an efficient solid-state battery or a room temperature superconductor.

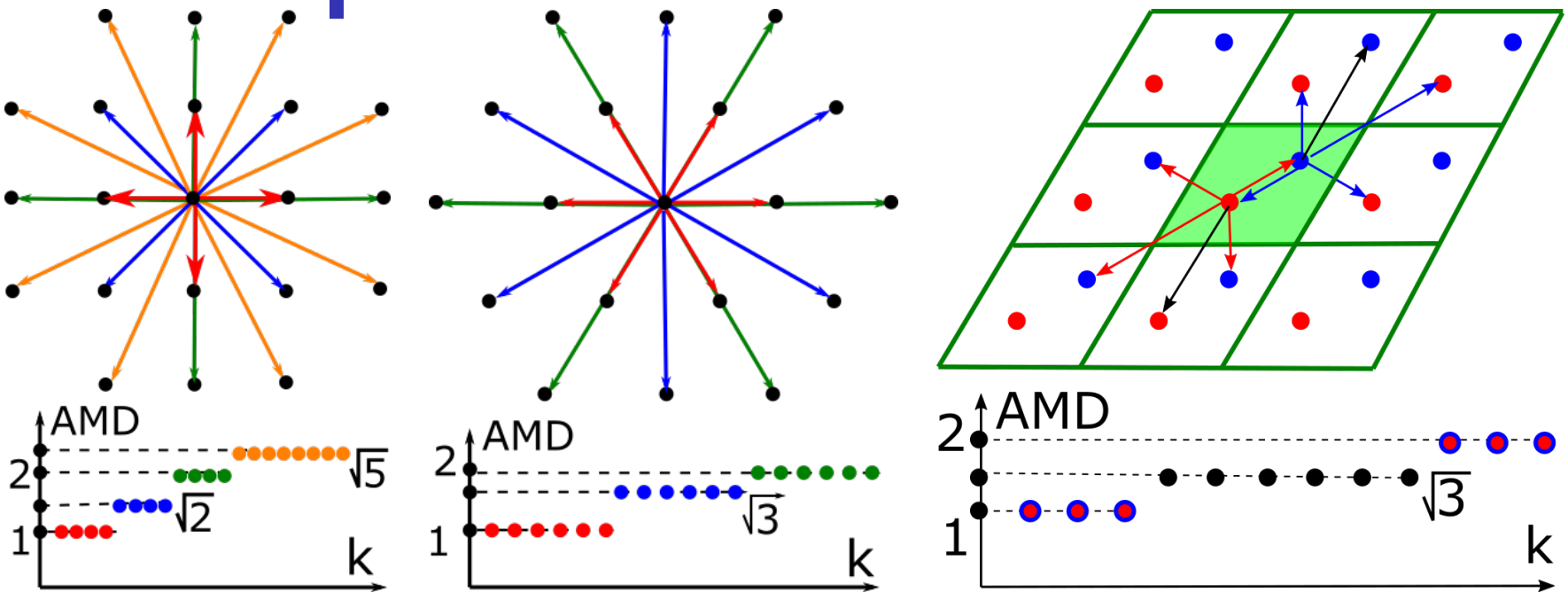
New isometry invariants of crystals

Distance-based invariants, arxiv:2009.02488
D.Widdowson, M.Mosca, A.Pulido, A.Cooper
+ simple, + continuous, + fast (near linear time, minutes on 5679 T2 crystals), - incomplete?

Density functions, with T. Heiss, SoCG 2021
+ continuous, + complete for generic crystals,
- slower (cubic time, hours on 5679 T2 crystals)

Isosets, DGMM 2021, arxiv.org:2103.02749
+ continuous, + complete for all crystals,
- slower (cubic time, to be implemented).

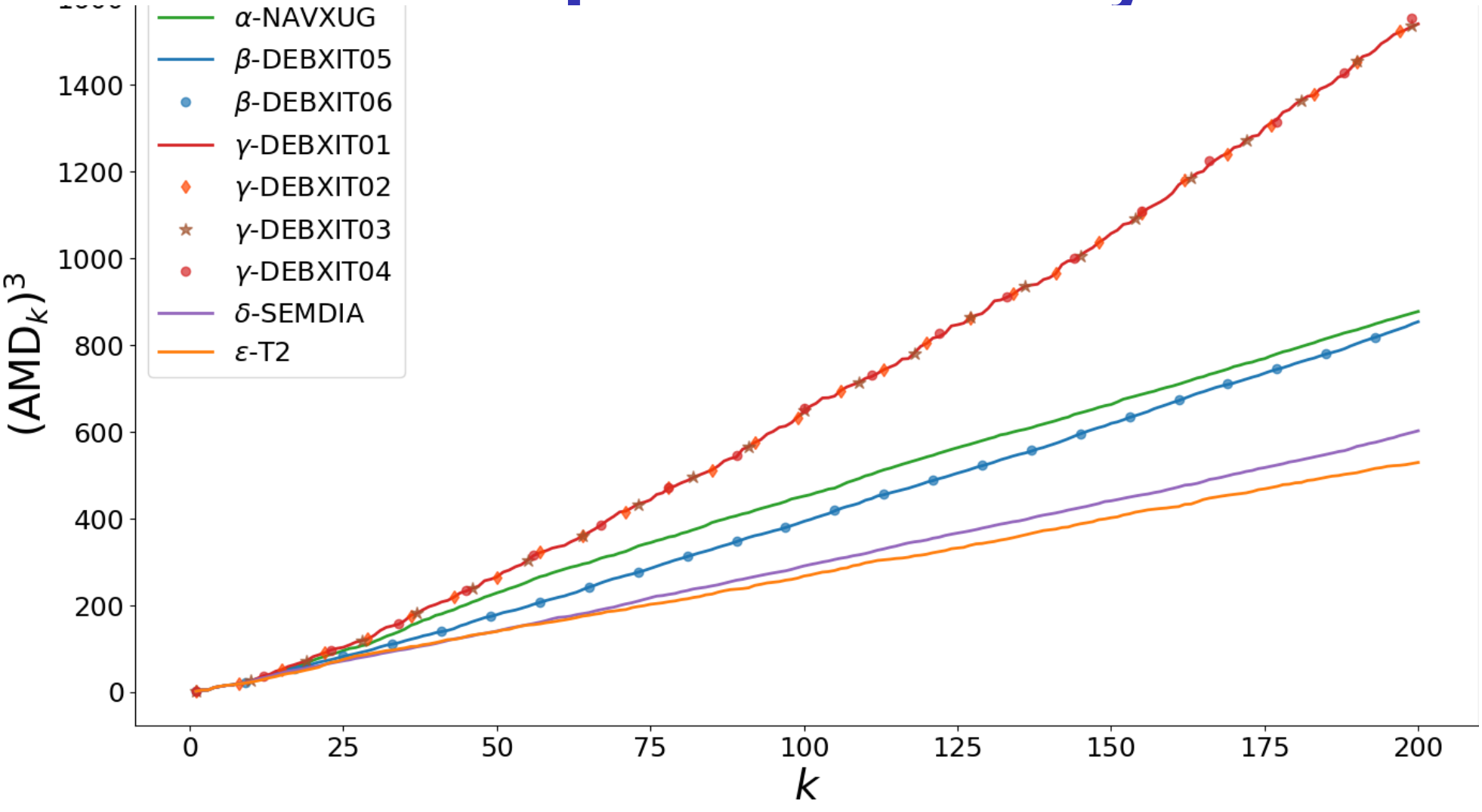
Sequence of AMD invariants



For a periodic point set $S \subset \mathbb{R}^n$, let d_{ij} be the distance from a point p_i in a motif, $i = 1, \ldots, m$, to its j-th nearest neighbour in S. For any $k \geq 1$,

Average Minimum Distance $\mathrm{AMD}_k = \dfrac{1}{m} \sum_{i=1}^{m} d_{ik}$.

AMD of experimental crystals



Nine T2 crystals split into five families α, β, γ, δ,

A tree of 12576 crystalline drugs