UNIVERSITY OF LIVERPOOL

LEVERHULME TRUST

The Leverhulme Research Centre for Functional Materials Design

Dense periodic packings in the light of crystal structure prediction

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Soft Packings, Nested Clusters, and Condensed Matter

3 October 2019

CCDC diamond Hartree Centre Science & Technology Facilities Council Imperial College London ICNS King Abdullah University of Science and Technology University of Southampton

Group in Topological Data Analysis

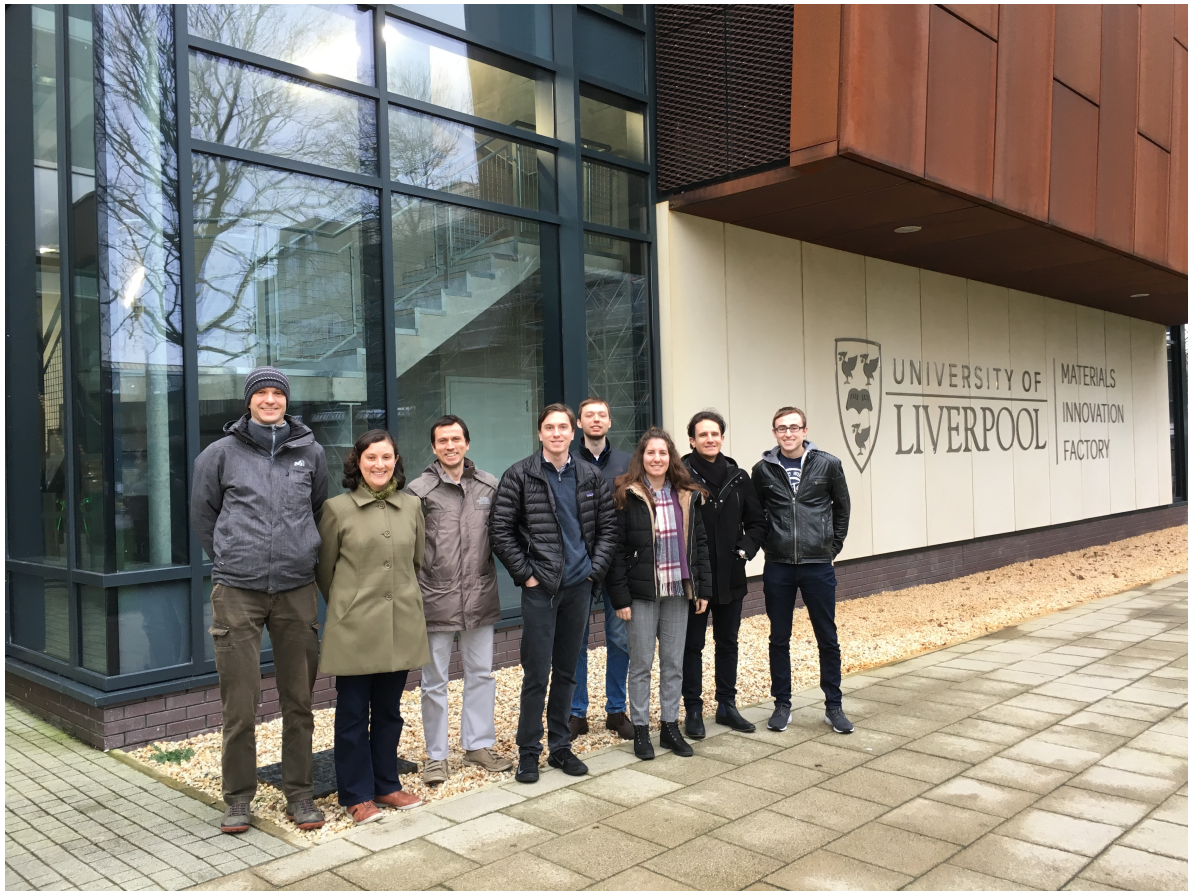


Table of Contents

MOTIVATION

Motivation

Molecular crystal

Crystal (IUCr)

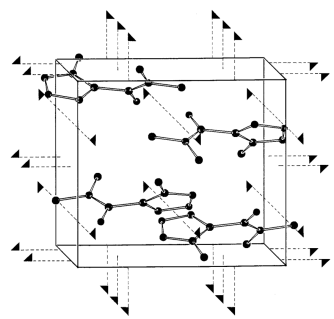
- A material is a crystal if it has essentially a sharp diffraction pattern.

Crystal

- A structure built of one or a few different kinds of discrete units, arranged in more or less modular fashion that extends infinitely.

Molecular Crystal

- The module is a space filling polyhedron (unit cell) containing molecules.



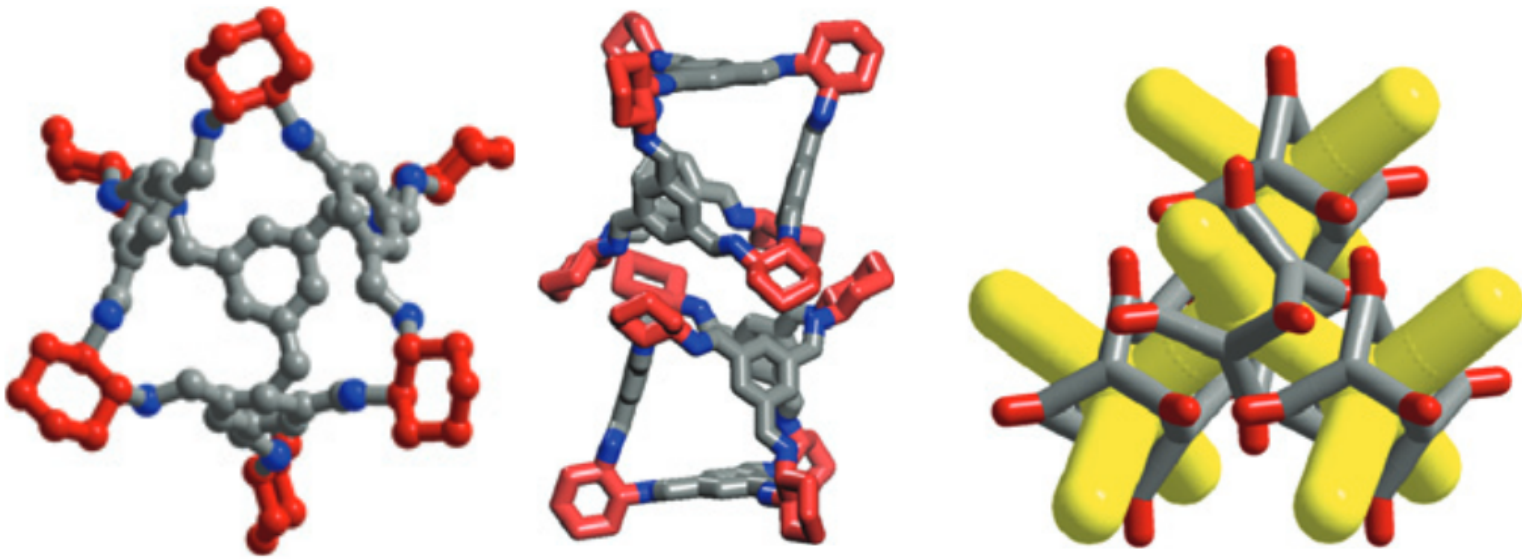
C. Giacovazzo et al., Fundamentals of Crystallography, 2011.

Motivation

Crystal structure prediction

- **Crystal structure prediction (CSP)** - The calculation of crystal structures of solids from first principles.
  - First principles = Quantum electrodynamics
- Calculations are based on:
  - **Density functional theory** - precise but computationally expensive.
  - **Force field methods** - approximations to the first principles but "fast" to compute (Lennard–Jones potential, Buckingham–Coulomb potential, . . .).

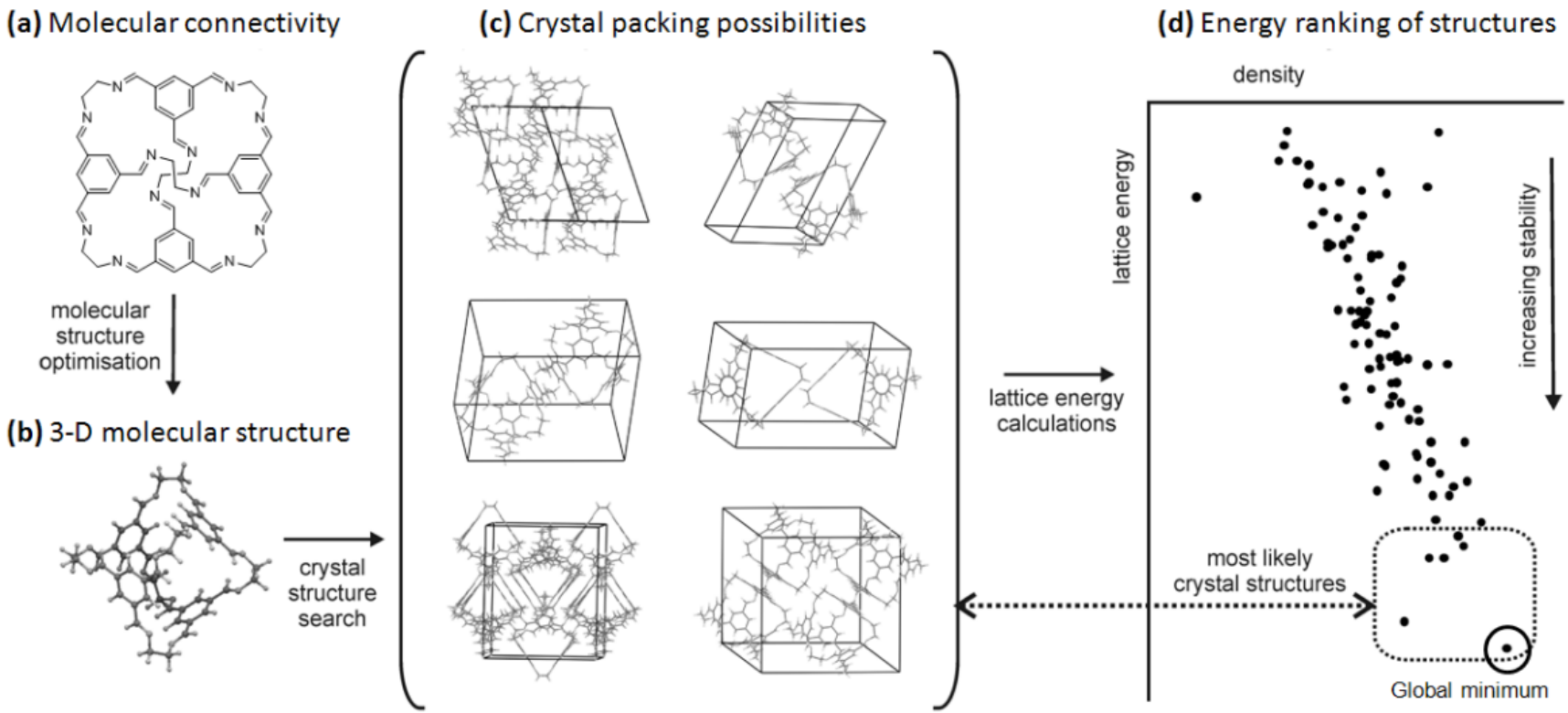
Porous organic cages (Cage 3)



Tozawa et al., Porous organic cages., Nat. Mater., 2009, 8, 973.

Motivation

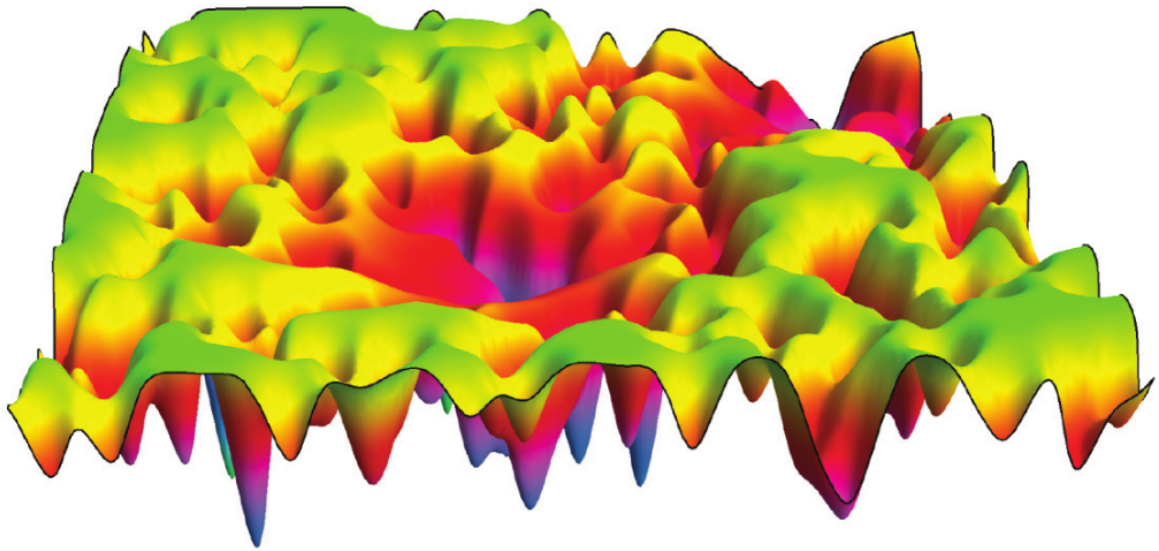
CSP work flow



G. M. Day and A. I. Cooper, Energy–Structure–Function Maps: Cartography for Materials Discovery, Advanced Materials, 2018, 30, 1704944.

Motivation

Energy landscapes



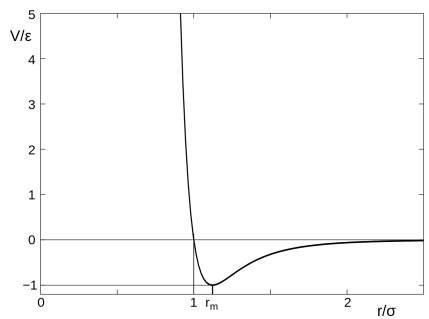
D. J. Wales, Exploring Energy Landscapes, Annu. Rev. Phys. Chem., 2018, 69,401.

Motivation

Lennard–Jones potential

$$U_{LJ} = 4\epsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^{6}}{r^{6}}\right) = \epsilon\left(\frac{{R_m}^{12}}{r^{12}} - \frac{2{R_m}^{6}}{r^{6}}\right)$$

- ϵ - Depth of the potential well.
- $\sigma = 2^{-1/6}R_m$ - The position where the repulsive branch crosses zero.
- r - The distance between two particles.
- $-\frac{2{R_m}^{6}}{r^{6}}$ - The attractive term.
- $\frac{{R_m}^{12}}{r^{12}}$ - The repulsive term.



https://en.wikipedia.org/wiki/Lennard-Jones_potential

Motivation

Lennard–Jones potential stationary points

Potential for atoms:

$$U_{LJ} = \sum_{i<j} 4\epsilon_{ij} \left(\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}} \right)$$

Potential for molecules:

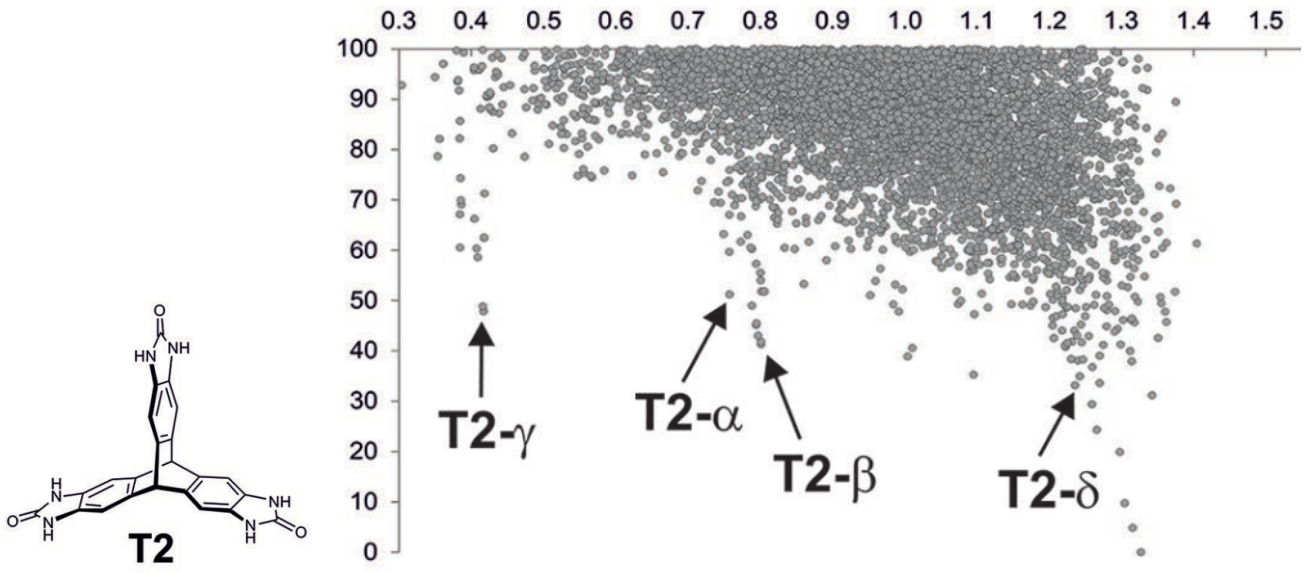
$$U_{LJ} = \sum_{a \in A} \sum_{b \in B} 4\epsilon_{ab} \left(\frac{\sigma_{ab}^{12}}{r_{ab}^{12}} - \frac{\sigma_{ab}^{6}}{r_{ab}^{6}} \right)$$

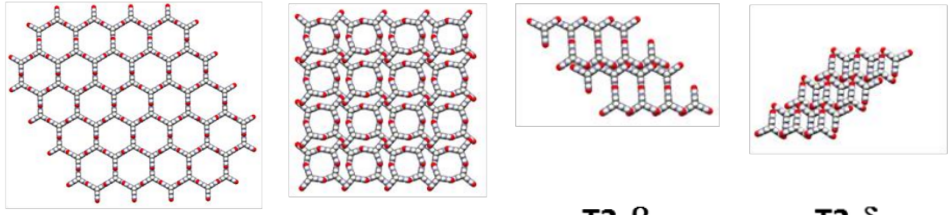
	Stationary point index															
N	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
4	1	1	2	1	1	0	0									
5	1	2	4	6	6	2	1	0								
6	2	3	13	24	30	26	16	5	1	0						
7	4	12	44	98	168	190	168	101	45	11	1	0				
8	8	42	179	494	1000	1458	1619	1334	852	388	125	26	1	0		
9	21	165	867	2820	6729	12 093	16 292	16 578	13 226	8286	4053	1444	376	56	1	0
10	64	635	4074	16 407	46 277	*97 183*										
11	170	2424	17 109	*47 068*												
12	515	8607	*27 957*													
13	1509	28 756	*88 079*													

P. K. Doye and D. J. Wales, Saddle points and dynamics of Lennard-Jones clusters, solids, and supercooledliquids, J. Chem. Phys., 2002, 116, 3777.

Motivation

CSP lattice energy landscape



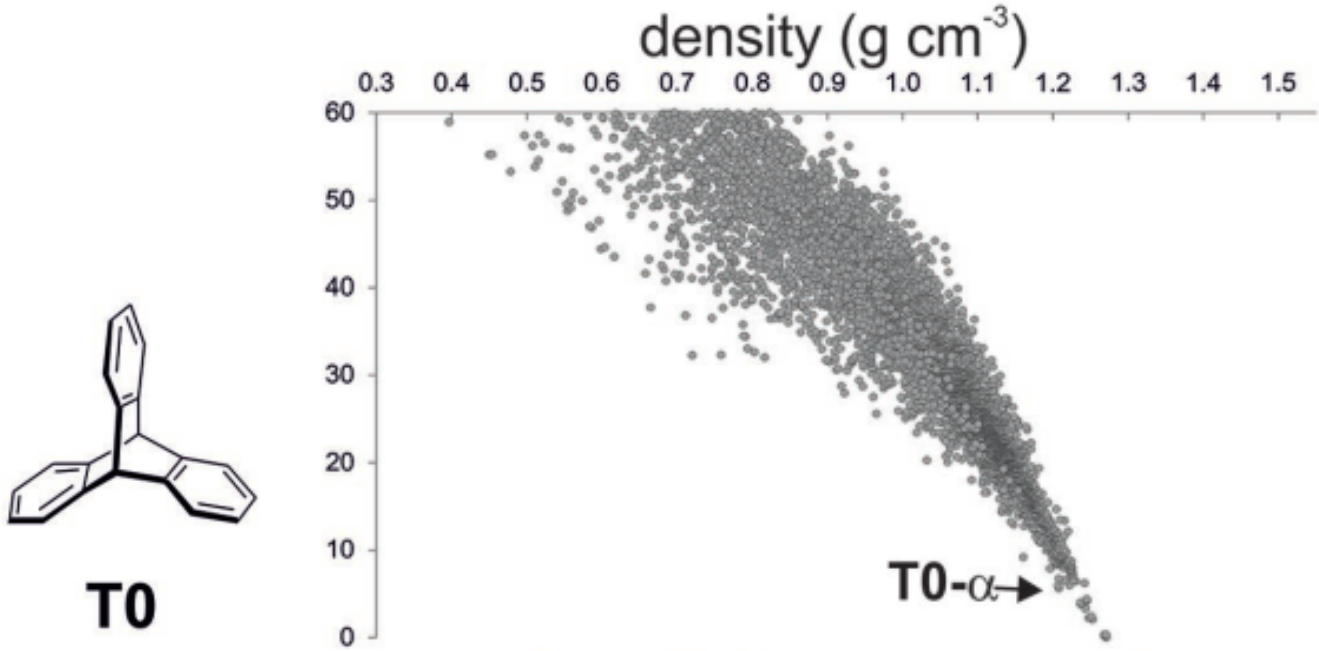


T2-γ (0.417 g cm^{-3}) T2-α (0.758 g cm^{-3}) T2-β (0.801 g cm^{-3}) T2-δ (1.236 g cm^{-3})

A. Pulido et al., Functional materials discovery using energy–structure–function maps, Nature, 2017, 543, 657

Observation:

- Dense packed structures tend to have lower energies.



T0 lattice energy landscape.

A. Pulido et al., Functional materials discovery using energy–structure–function maps, Nature, 2017, 543, 657.

Motivation

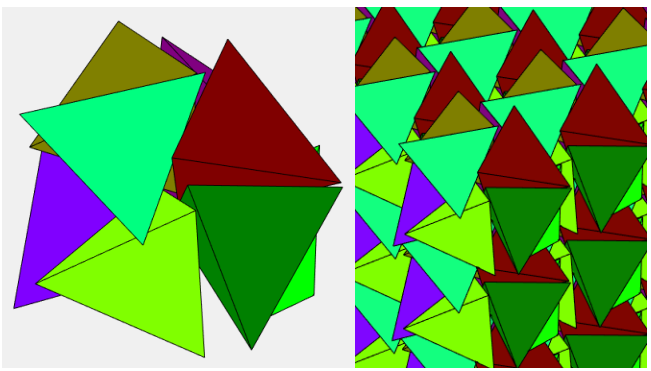
Periodic packing

A periodic packing $\mathcal{K}_P$ is a system of translates and rotations of a given set K, that is

$$\mathcal{K}_P = \{R_i K + \mathbf{a_i} + \mathbf{b_j} \mid i = 1, 2, \ldots, N;\ j = 1, 2, \ldots\}$$

if it is a packing into the whole space.

- $\mathbf{a_1}, \mathbf{a_2}, \ldots, \mathbf{a_N}$ are elements of a unit cell
- $\mathbf{b_1}, \mathbf{b_2}, \ldots$ are elements of a lattice
- $R_1, R_2, \ldots, R_N \in SO(n) = \{A \in \mathbb{R}^{n \times n} : A^T A = I,\ \det A = 1\}$.



(a) (b)

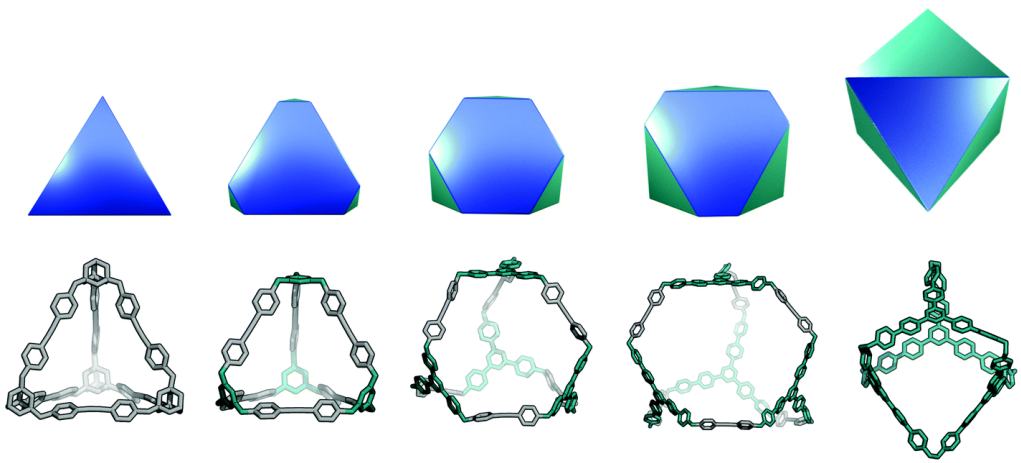
(a) A packing of 8 tetrahedra in a unit cell forming a module. (b) Periodic packing based on this module.

Problem:

- Find a reasonable geometric approximation of a molecule by a polyhedron K.
- Find dense molecular packings by optimizing periodic packing density ρ:

$$\rho = \frac{N\texttt{vol}(K)}{\texttt{vol}(\text{Unit cell})}.$$

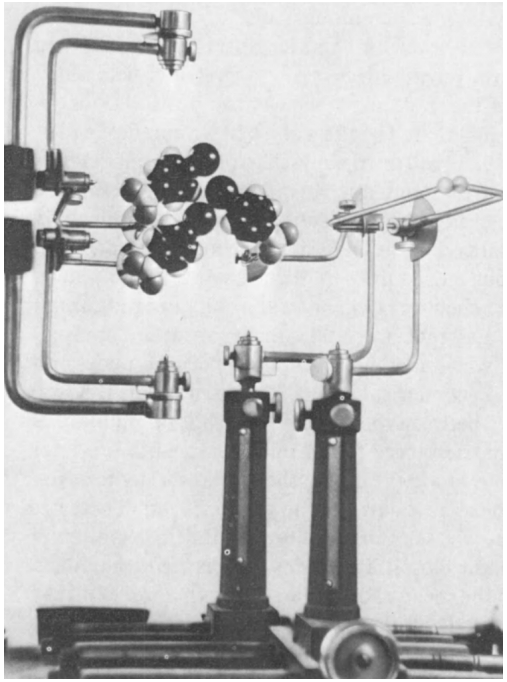
- Use the resulting structures as starting positions in CSP.



Santolini et al., Topological landscapes of porous organic cages, Nanoscale, 2017, 9, 3280.

Motivation

Structure seeker



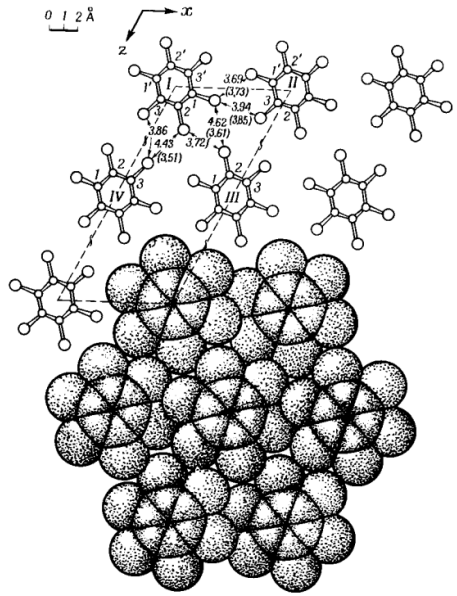


Fig. 3. Projection xOz of hexachlorobenzene structure.

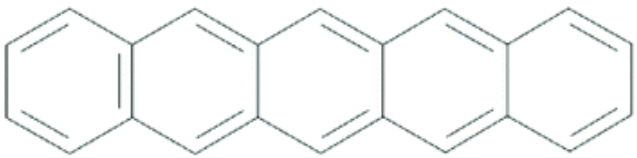
A. I. Kitaigorodsky, Molecular crystals and Molecules, 1973, Academic Press.

PRELIMINARY RESULTS

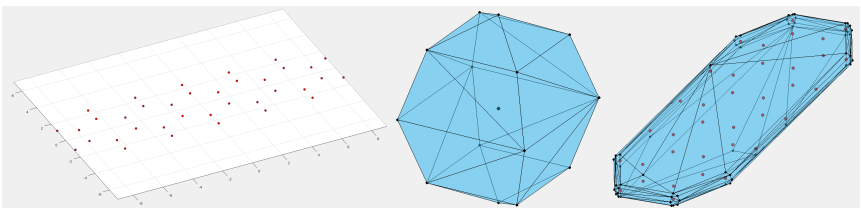
Preliminary results

Pentacene modelling

- Around every pentacene atom we put 14 points uniformly placed on a sphere with the radius 0.5573/2.
- Computed the convex hull of the resulting point cloud.
- Resulting polyhedron defined by a triangulation with 58 vertices, 112 edges, 168 faces.



(a)



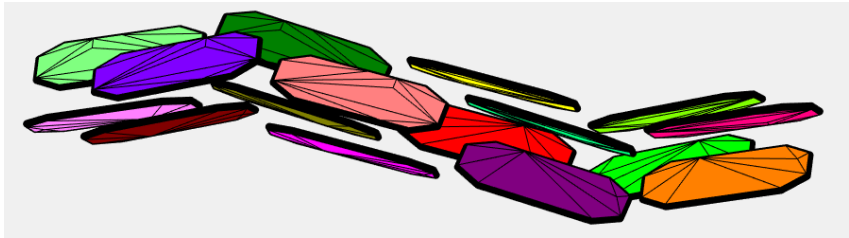
(b) (c) (d)

(a) Pentacene. (b) Centers of atoms of pentacene. (c) 14 points placed on a sphere with radius 0.5573/2. (d) Convex hull of the resulting point cloud with centres of pentacene atoms inside (red).

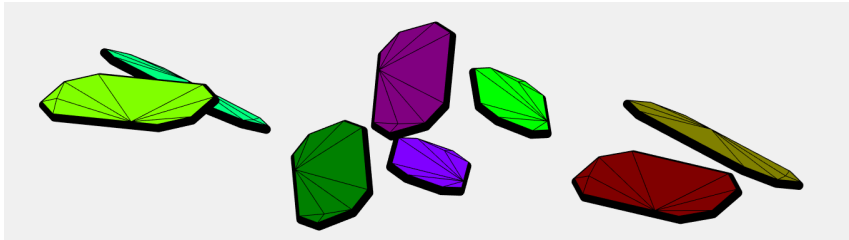
Preliminary results

Pentacene modelling

- The radius was computed from a CSP dataset containing 586 pentacene structures, where minimum euclidean distance between pentacene molecules within every crystal structure was computed.



(a)



(b)

(a) A model of the pentacene crystal structure from the CSP dataset. (b) The crystal structure where the minimum distance between two pentacene molecules is attained.

Preliminary results

Monte-Carlo molecular dynamics simulations

Problem statement:

Find a periodic packing $\mathcal{K}_{\text{min}}$ of a given set K that minimizes the volume of the unit cell

$$\mathcal{K}_{\text{min}} = \arg\min_{\mathcal{K}_P} \texttt{vol}(\text{Unit cell})$$

subject to no intersection constraint,

$$K_i \cap K_j = \emptyset \ (i \neq j).$$

First approach:

- Stochastic optimization methods - problem exploration.
- Molecular dynamics simulations - periodic boundary conditions.
- Well explored approach.
- For example by Salvatore Torquato and Yang Jiao.

S. Torquato and Y. Jiao, Dense packings of polyhedra: Platonic and Archimedean solids, Phys. Rev. E, vol. 80, 2009.

J. A. Andersona, M. E. Irrgangb, S. C. Glotzer, Scalable Metropolis Monte Carlo for simulation of hard shapes, Computer Physics Communications, vol. 204, 21, 2016.

Preliminary results

Simulated annealing periodic packing algorithm

Input:

- Polyhedron specifications - Vertices, edges and faces.
- Initial configuration of the system. -

Algorithm:

- At each step s
  - Let the system of N 3–polytopes evolve randomly subject to periodic boundary conditions.
  - Apply standard simulated annealing acceptance rate to the unit cell contraction/expansion.

$$P(\mathcal{K}_t \leftarrow \mathcal{K}_{new}) = \begin{cases} 1 & \text{if } \Delta\rho > 0 \\ e^{\frac{-\Delta\rho}{T_t}} & \text{if } \Delta\rho \leq 0 \end{cases}$$

where $\Delta\rho = \rho(\mathcal{K}_{new}) - \rho(\mathcal{K}_t)$.

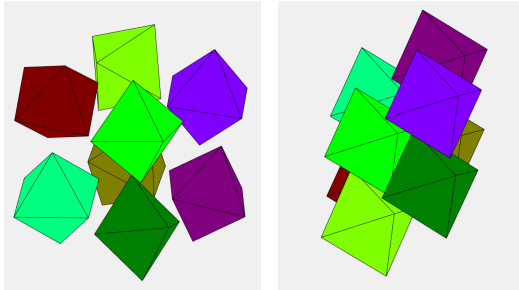
Output:

- Density, unit cell parameters, coordinates and rotations of all particles in the unit cell.

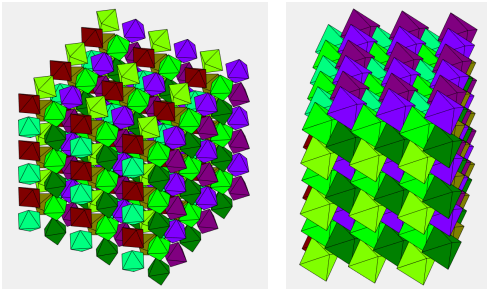
Preliminary results

Octahedra packing

Left:Initial density 0.1667, **Right**: Output density 0.9178.



Single unit cell

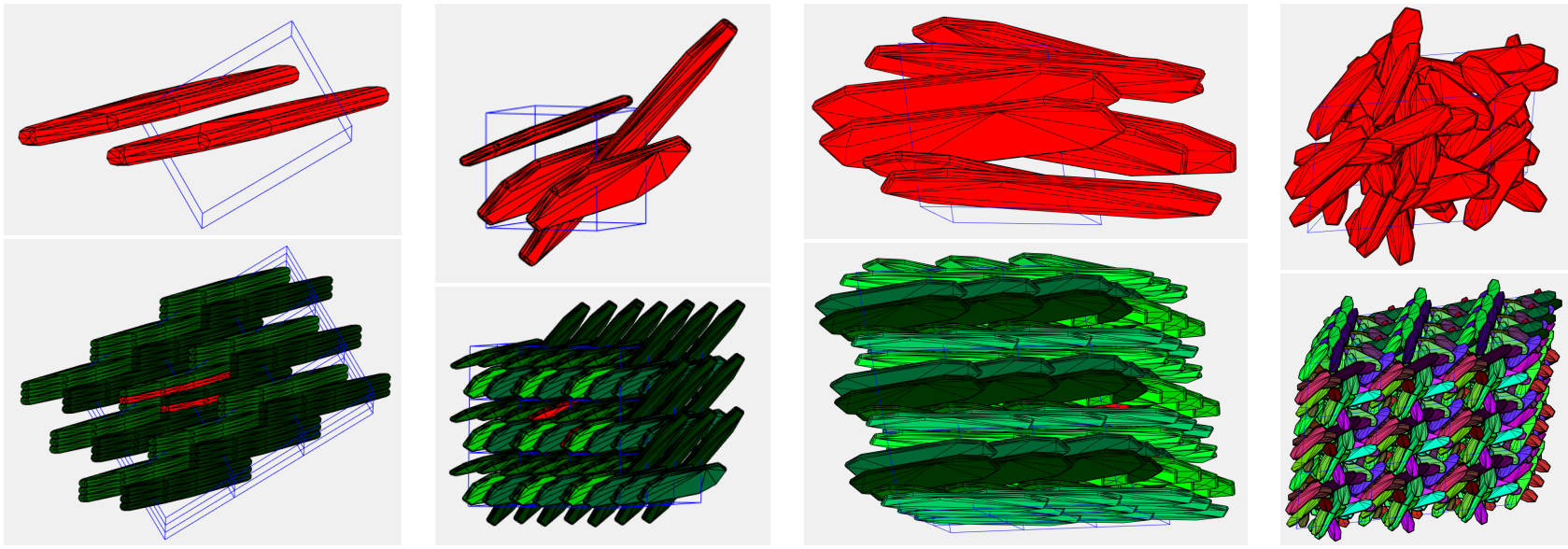


27 unit cells

Optimal lattice packing density 0.9474.

Preliminary results

Pentacene packings



(a) (b) (c) (d)

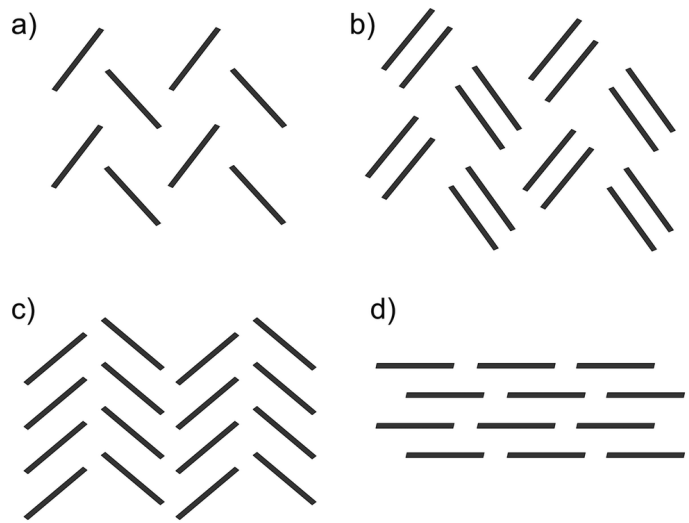
Densities of packings of (a) 2 $\rho \approx 1$, (b) 4 $\rho = 0.8093$ (c) 8 $\rho = 0.6940$ and (d) 54 $\rho = 0.1521$ pentacene models.

FUTURE DIRECTIONS

Future directions

Modelling

- Pentacene has 4 main packing types.
- Simulated annealing periodic packing algorithm $\rightarrow \beta$



(a) herringbone; (b) sandwich herringbone; (c) γ and (d) sheet (β).

J. E. Campbell et al., Predicted energy–structure–function maps for the evaluation of small molecule organic semiconductors., J. Mater. Chem. C, 2017, 5, 7574.

Dense periodic space group packings

- Reduce the number of parameters to:
  - Unit cell parameters.
  - Position and rotation of one polyhedron in the unit cell.
- Positions of all other polyhedra are given by the space groups symmetries.

Definition (Crystal pattern)

An object in n-dimensional point space E^n is called an n-dimensional crystallographic pattern or, for short, *crystal pattern* if among its symmetry operations

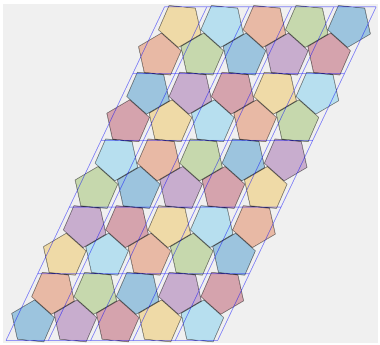
1. there are n translations, the translation vectors $t_1, \ldots, t_n$ of which are linearly independent,
2. all translation vectors, except the zero vector $\mathbf{o}$, have a length of at least $d > 0$.

Definition (Space group)

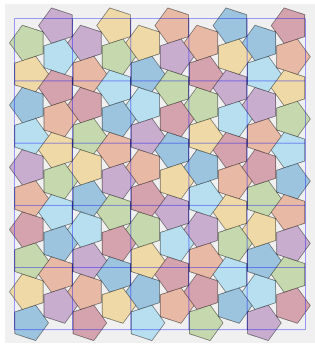
The symmetry group of a three-dimensional crystal pattern is called its space group.

International Tables for Crystallography Volume A: Space-Group Symmetry, Ed. T. Hahn, 2005.

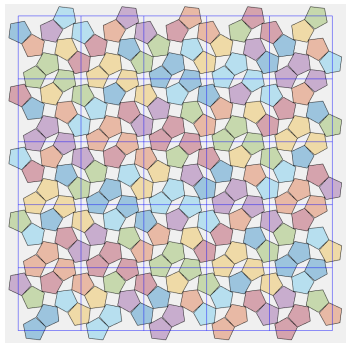
First steps in plane groups



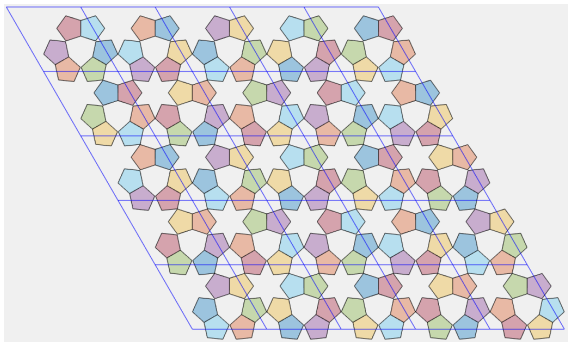
(a) p2



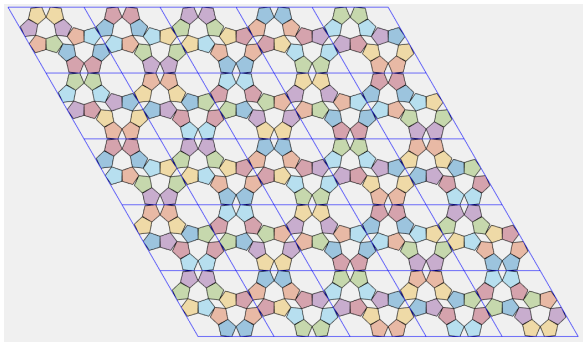
(b) p2gg



(c) p4gm



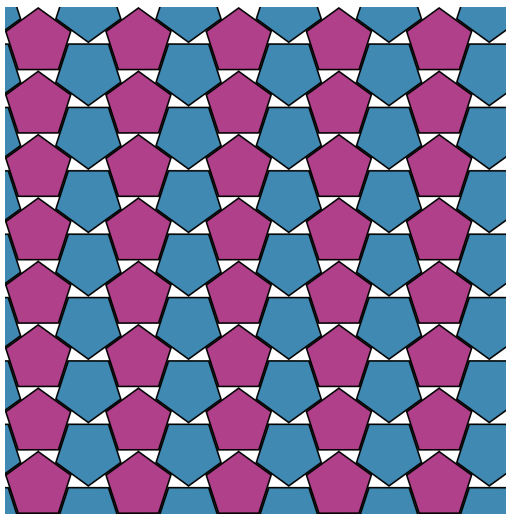
(d) p3m1



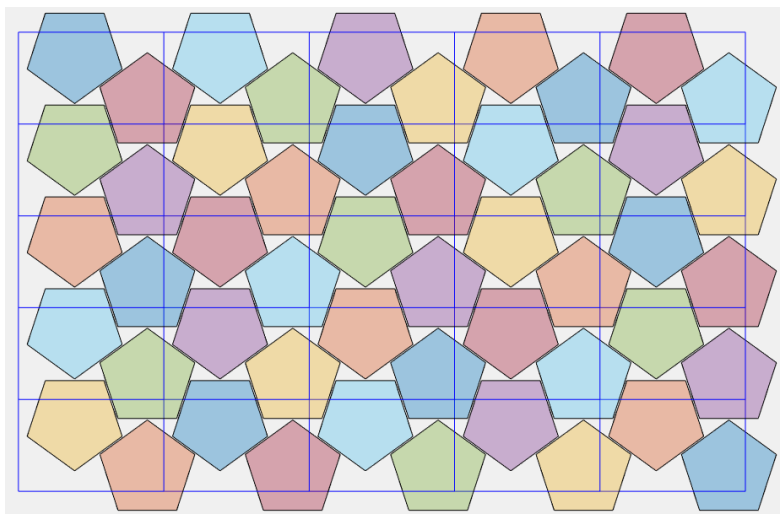
(e) p6mm

Packings of pentagons using genetic algorithm.

Densest packing of pentagons



(a) Pentagonal ice-ray



(b) pg

https://commons.wikimedia.org/w/index.php?title=File:2-d_pentagon_packing_dual.svg&oldid=260319594

Future directions

Information-geometric optimization

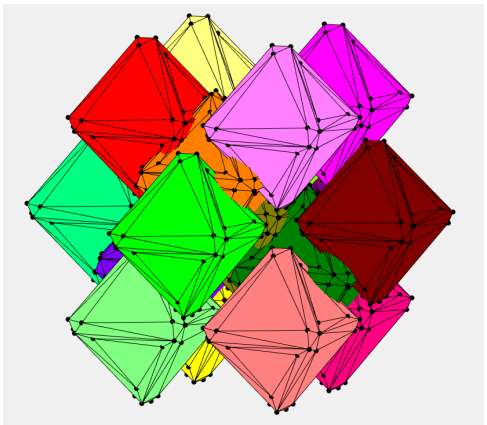
- We want our packing procedure to be applicable to different shapes and different space groups.
  - **Question**: Is there an optimal packing algorithm for an arbitrary convex set and arbitrary space group?
- No free lunch theorem $\rightarrow$ Trade off between generality of an optimization algorithm on a set of problems and its performance.
- Experiments so far show that stochastic optimization methods work reasonably well.
- Continue to explore stochastic optimization approaches.
- Transfer function $f(x)$ to be optimized to a function $F(\theta)$ defined on the space of probability measures and then perform a natural gradient descent over $F(\theta)$ with respect to the (quadratic) Wasserstein metric.

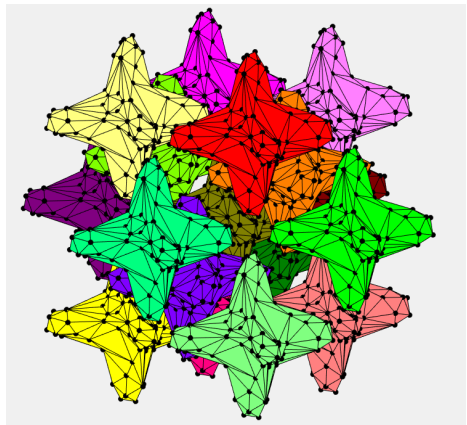
Y. Ollivier et al., Information-Geometric Optimization Algorithms: A Unifying Picture via Invariance Principles, Journal of Machine Learning Research, 2017, 18.

Future directions

Packing of concave polytopes

- Convex hulls of the organic cage molecule crystal structure overlap.
- Spectrum of α-shapes $\rightarrow$ There exists α for which the shapes do not overlap but $\alpha + \epsilon$ there is an overlap for some small ϵ.
- Overlap checks for concave sets are necessary.





THANK YOU

APPENDIX

Future directions

Simulated annealing periodic packing algorithm

Algorithm:

- For N number of stages do
  - For M number of cycles do
    - For every polyhedron in a unit cell
      - With probability p translate the polyhedron in a random direction within the unit cell or with $1 - p$ rotate the polyhedron around a random axis by a random angle.
      - Repeat until the constrains are satisfied or until J number of attempts.
  - With probability p_u contract the unit cell or with the probability $1 - p_u$ expand the unit cell by a random strain tensor. Repeat until success or until L number of attempts.
  - Accept the new unit cell configuration $\mathcal{K}_{new}$ with probability

$$P(\mathcal{K}_t \leftarrow \mathcal{K}_{new}) = \begin{cases} 1 & \text{if } \Delta\rho > 0 \\ e^{\frac{-\Delta\rho}{T_t}} & \text{if } \Delta\rho \leq 0 \end{cases}$$

where $\Delta\rho = \rho(\mathcal{K}_{new}) - \rho(\mathcal{K}_t)$.