UNIVERSITY OF LIVERPOOL

LEVERHULME TRUST

The Leverhulme Research Centre for Functional Materials Design

Dense periodic packings in the light of crystal structure prediction

Miloslav Torda
Yannis Goulermas
Vitaliy Kurlin
Graeme M. Day
Linjiang Chen

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

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MOTIVATION

Definition

1. A crystal is a solid that has long-range positional order.
2. Long-range positional order can be inferred from the existence of Bragg peaks in the Fourier spectrum of the solid.

R. Lifshitz, What is a crystal?, Z. Kristallogr., 2007, 222, 313-317.

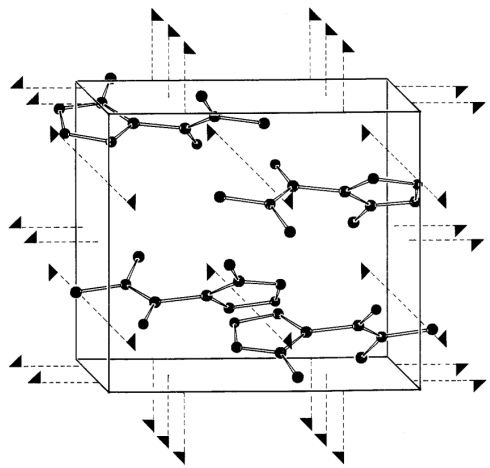
Periodic crystal

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

M. Senechal, Crystalline Symmetries: An informal mathematical introduction., 1990.

Molecular Crystal

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



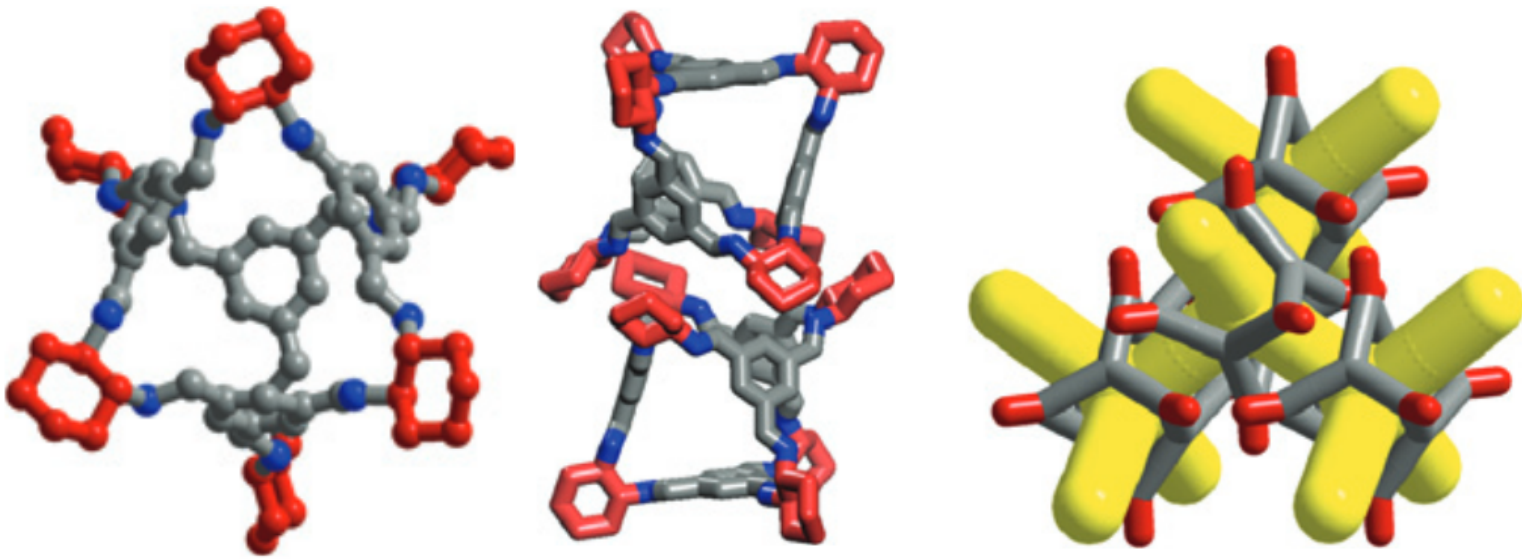
C. Giacovazzo et al., Fundamentals of Crystallography, 2011.

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, . . .).

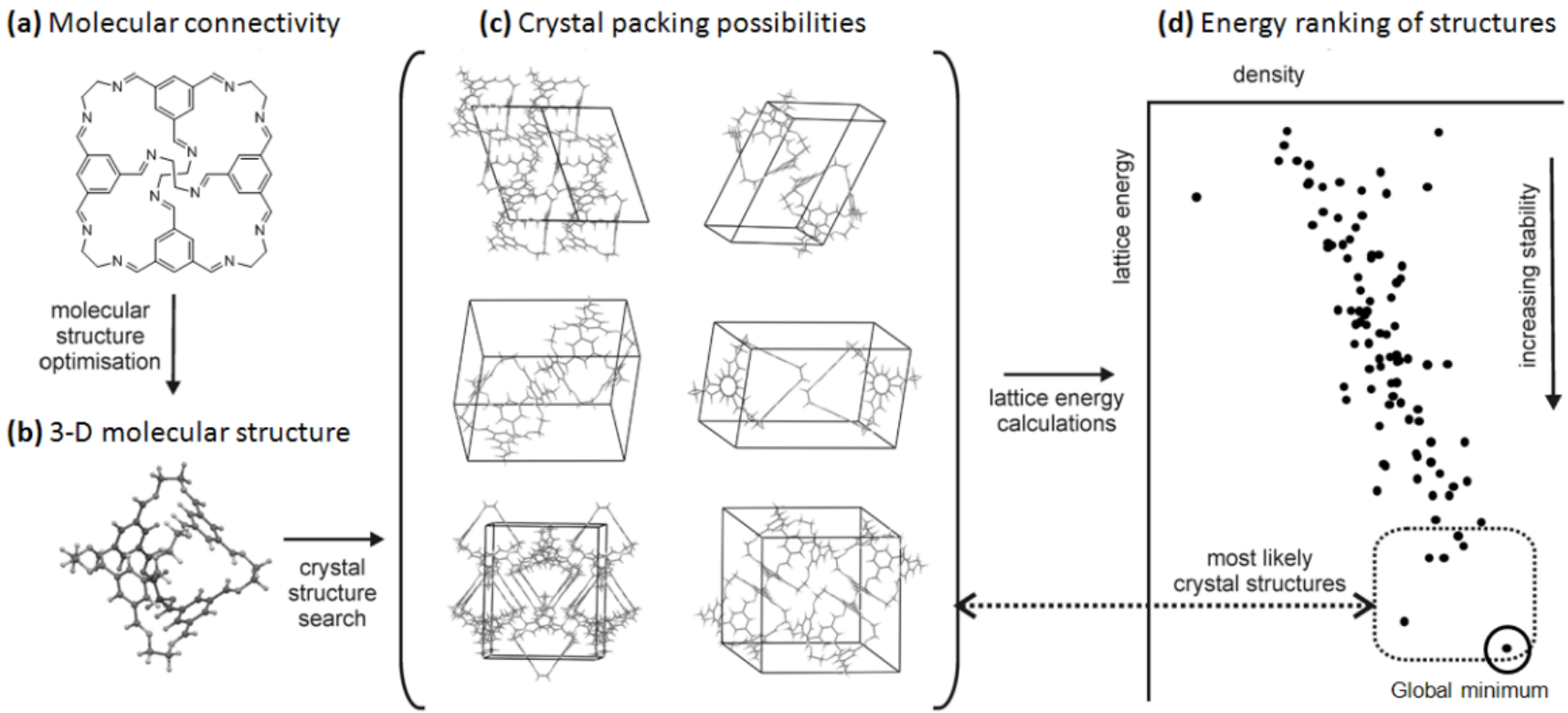
Porous organic cages (Cage 3)



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

Motivation

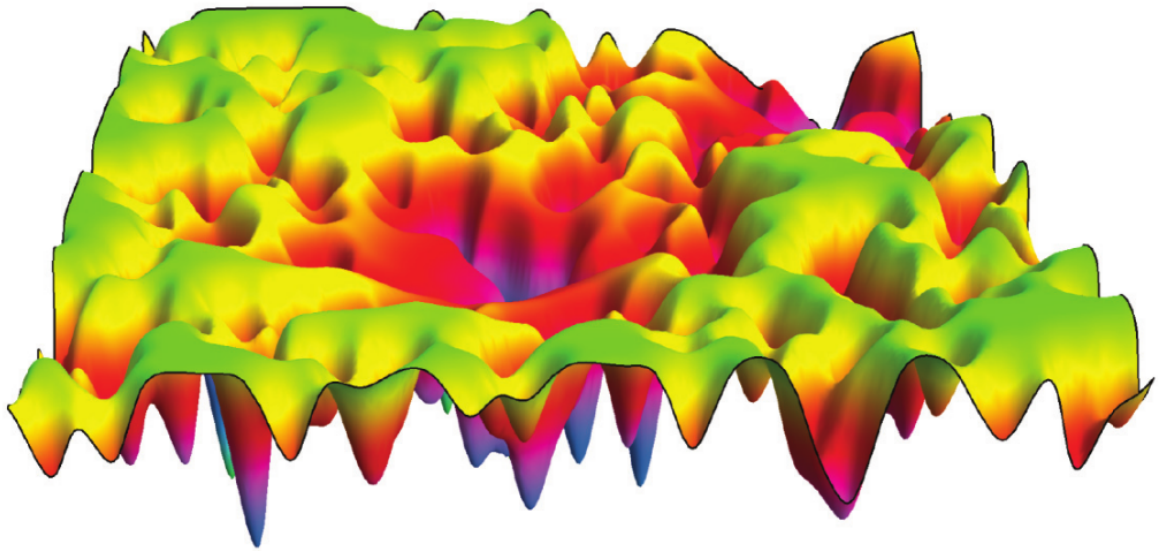
CSP work flow



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

Motivation

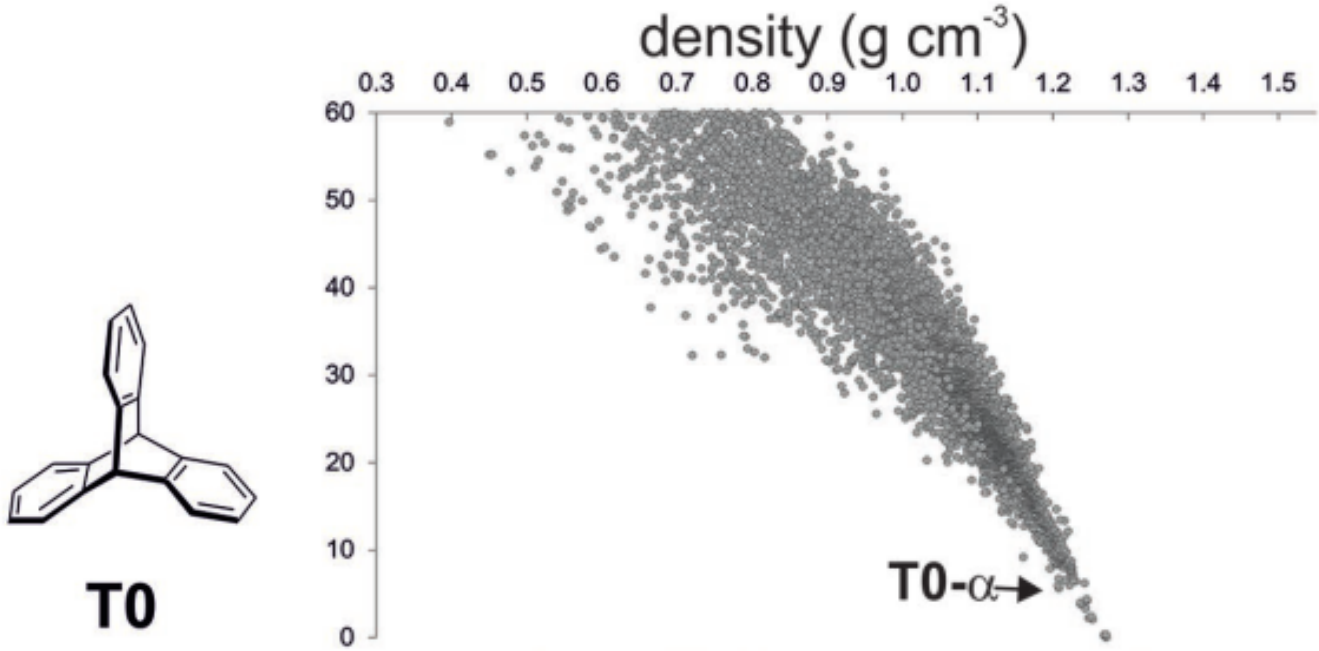
Energy landscapes



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

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

Packing problems

- Problems in discrete geometry that ask: What is the configuration of congruent copies of a given body K such that the ratio between the filled and the unfilled space is as large as possible.
- Famous example is the **Kepler conjecture**: *No arrangement of equally sized spheres filling space has a greater density than that of the FCC and HCP arrangements.*

BODY
Circular disk in $\mathbb{E}^2$
Parallel body of a rectangle
Intersection of two congruent circular disks
Centrally symmetric n-gon (algorithm in $O(n)$ time)
Ball in $\mathbb{E}^3$
Ball in $\mathbb{E}^8$
Ball in $\mathbb{E}^{24}$
Truncated rhombic dodecahedron in $\mathbb{E}^3$

Bodies K for which the optimal packing is known.

C. D. Toth, J. O'Rourke, J. E. Goodman eds., Handbook of Discrete and Computational Geometry., 2017.

Motivation

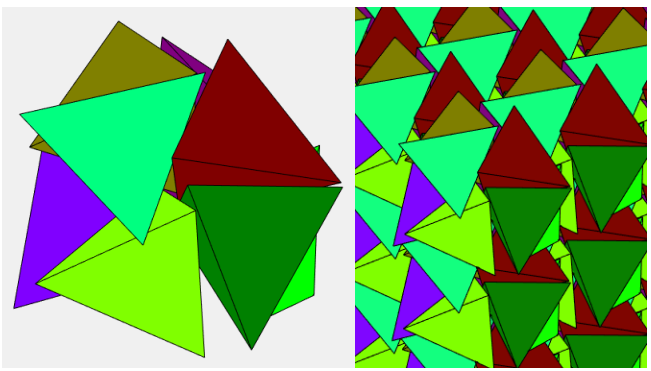
Periodic packing

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
- $R_1, R_2, \ldots, R_N \in SO(n) = \{A \in \mathbb{R}^{n \times n} : A^T A = I,\ \det A = 1\}$.



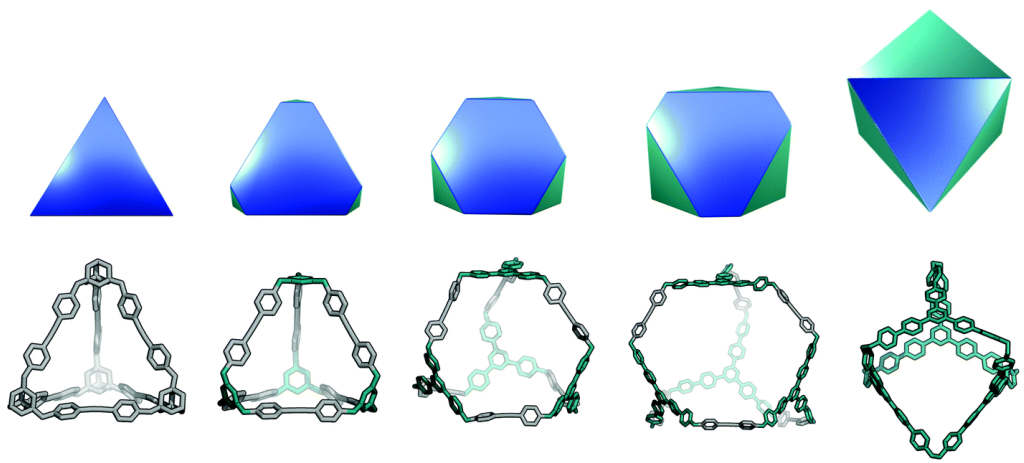
(a) (b)

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

Problem:

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

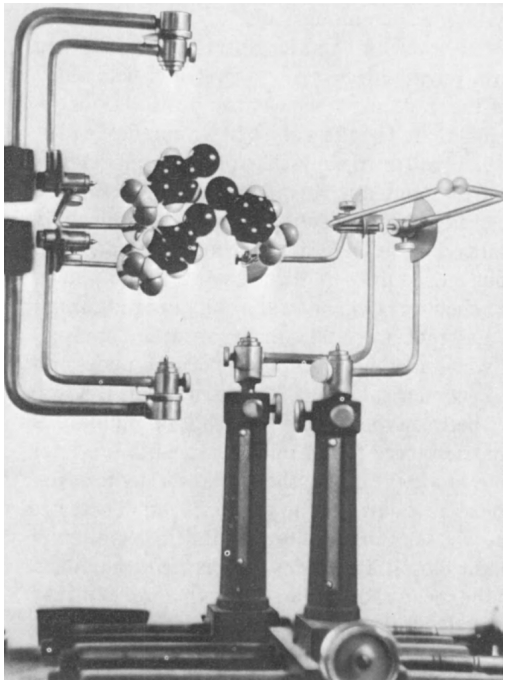
$$\rho = \frac{N\texttt{vol}(K)}{\texttt{vol}(\text{Unit cell})}.$$



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

Motivation

Structure seeker



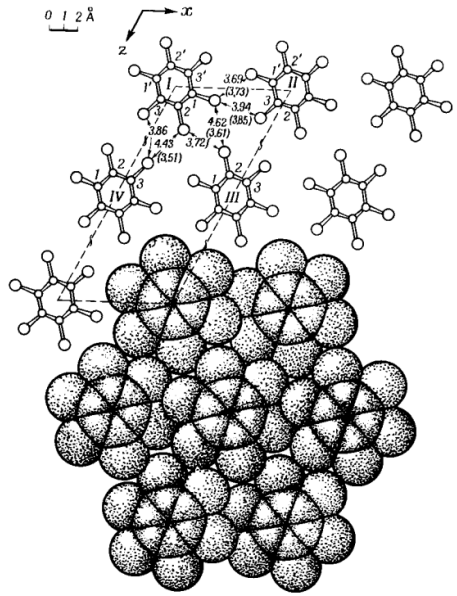


Fig. 3. Projection xOz of hexachlorobenzene structure.

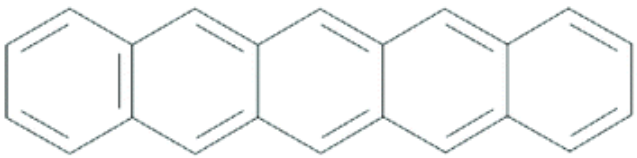
A. I. Kitaigorodsky, Molecular crystals and Molecules, 1973, Academic Press.

PRELIMINARY RESULTS

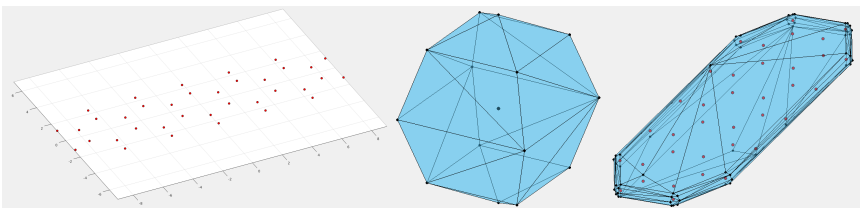
Preliminary results

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)



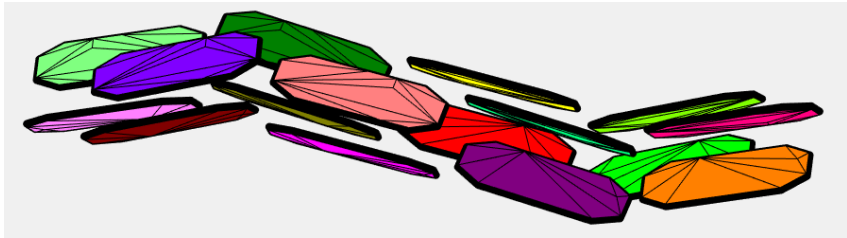
(b) (c) (d)

(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).

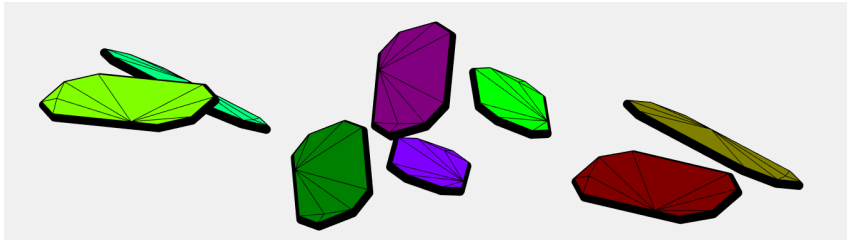
Preliminary results

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.

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

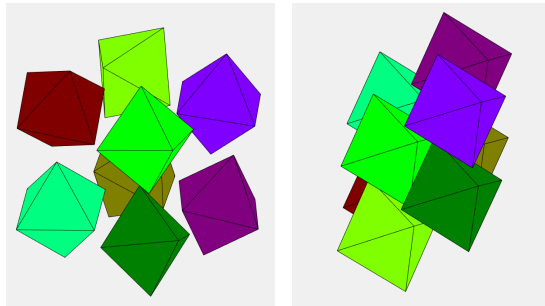
Output:

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

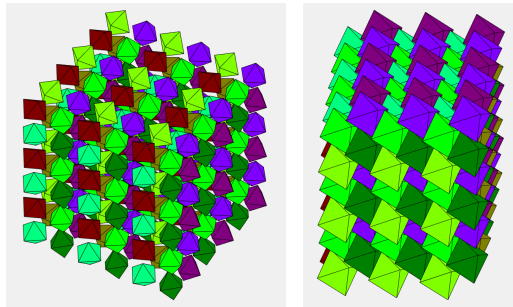
Preliminary results

Octahedra packing

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



Single unit cell

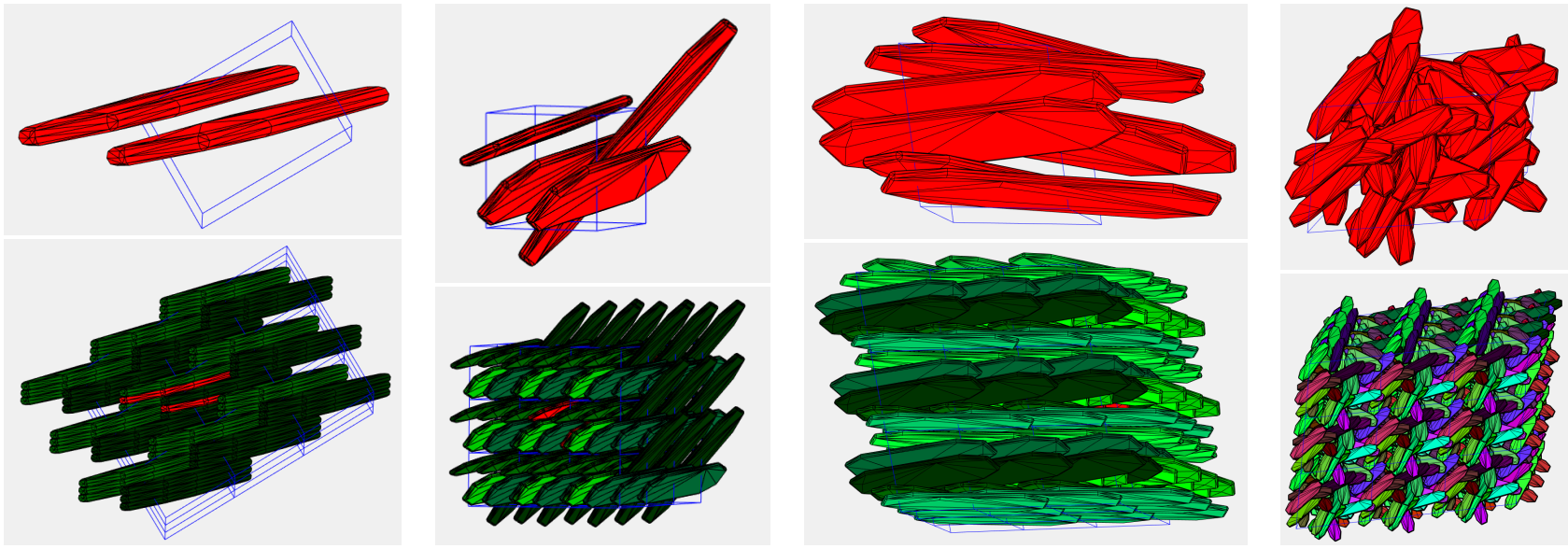


27 unit cells

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.

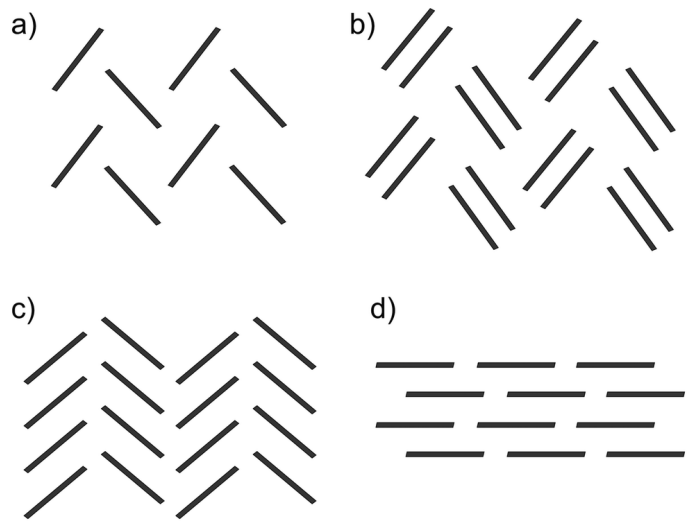
FUTURE DIRECTIONS

Future directions

Modelling

Problem

- 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.

Solution

Definition (Space group)

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

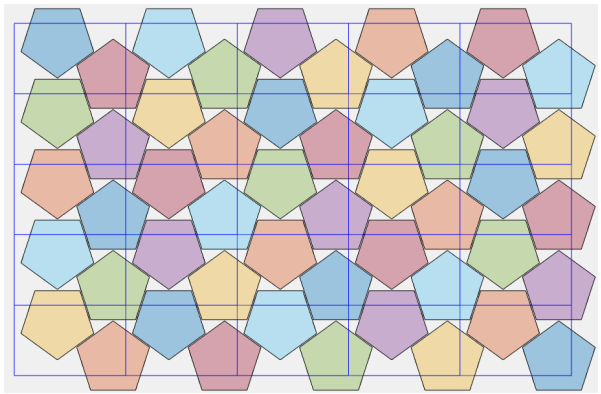
Definition (Crystal pattern)

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

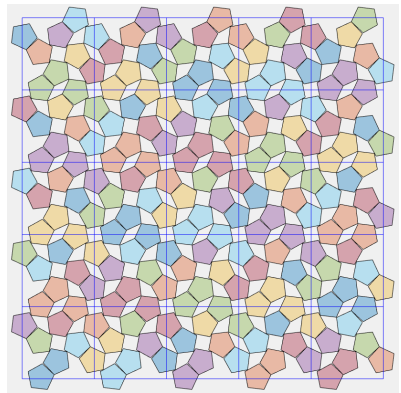
1. there are n translations, the translation vectors $t_1, \ldots, t_n$ of which are linearly independent,
2. all translation vectors, except the zero vector $\mathbf{o}$, have a length of at least $d > 0$.

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

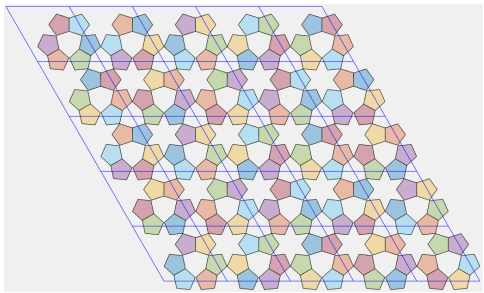
Plane groups packings of pentagons



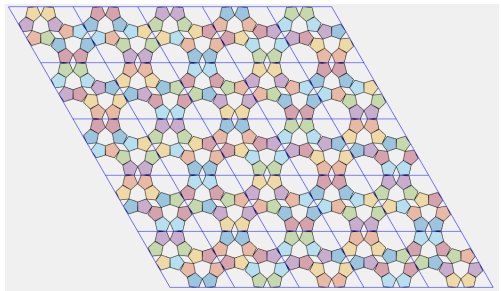
(a) pg



(b) p4gm



(c) p3m1



(d) p6mm

Packings of pentagons using genetic algorithm.

Future directions

Optimization method

Problem:

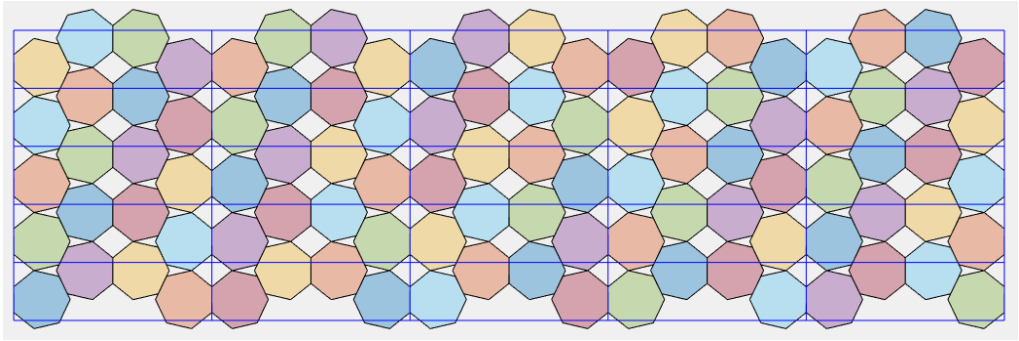
- Most of the results of optimal packings were obtained by ad hoc methods.
- We want our packing procedure to be more general: variety of bodies and space groups.
- Although the objective function is smooth, the constrains are not differentiable.

Solution:

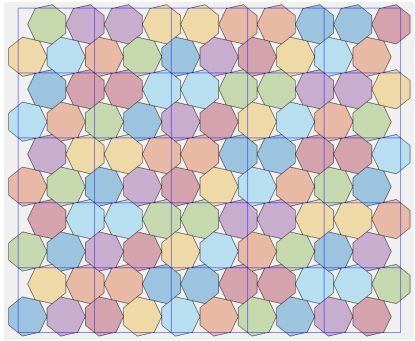
- Transfer function $f(x)$ to be optimized to a function $F(\theta)$ defined on the space of probability measures and then perform a natural gradient descent of $F(\theta)$ over a statistical manifold.

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

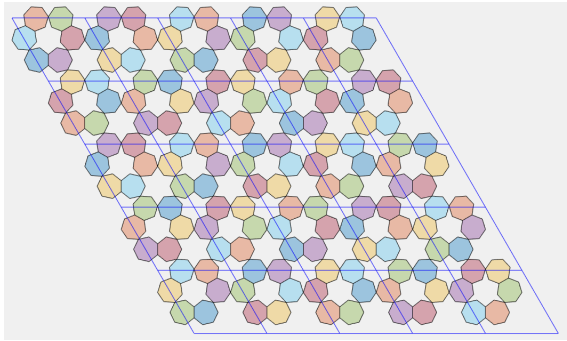
Plane groups packings of heptagons



(a) cm



(b) p2gg



(c) p3m1

Packings of heptagons using xNES.

THANK YOU