UNIVERSITY OF LIVERPOOL

LEVERHULME TRUST

The Leverhulme Research Centre for Functional Materials Design

Periodic packings in the light of crystal structure prediction.

First Year Progress Report

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MOTIVATION

Motivation

Crystal structure prediction

- **Crystal** - A structure built of one or a few different kinds of discrete units, arranged in more or less modular fashion.
- **Crystal structure prediction (CSP)** - The calculation of crystal structures of solids from first principles (QED).
- In principle an optimization problem of finding structures with minimal lattice energy.
- Calculations are based on
  - Force field methods.
  - Density functional theory.

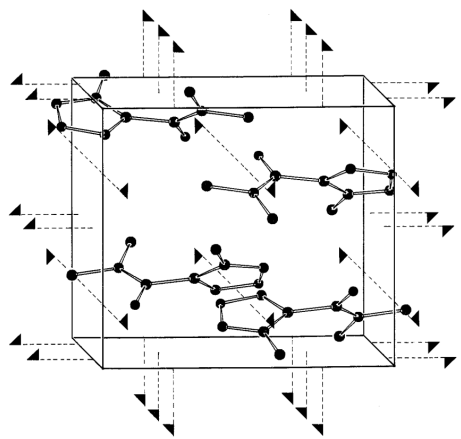


Figure: Example of a molecular crystal module

Motivation

Energy vs. density

- Dense packed structures tend to have lower energies

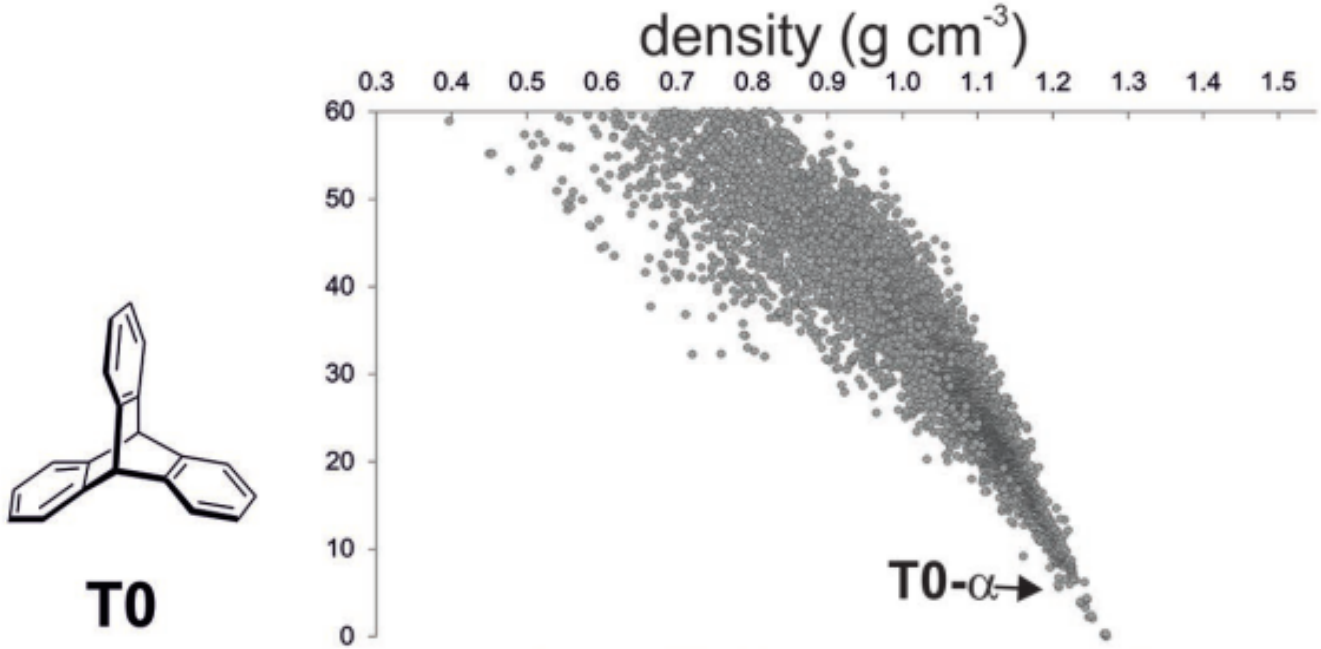
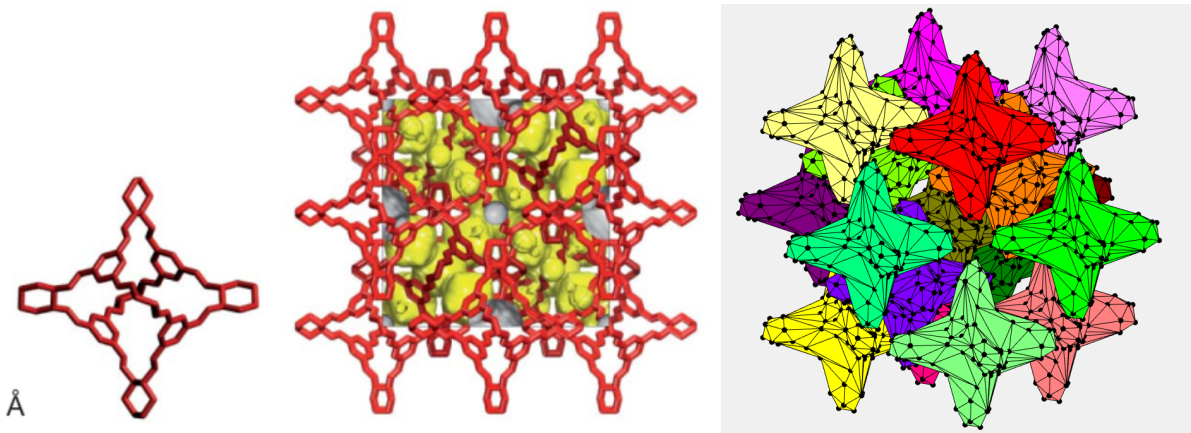


Figure: T0 CSP Lattice energy landscape

Motivation

Molecular packings

- Find dense packings of molecules approximated by polyhedra.
- Optimize packing density instead of energy.
- Use the resulting structures as starting positions in CSP.



(a) (b)

Figure: (a) Organic cage molecule 3 crystal structure. (b) α-shape of organic cage molecule 3.

PACKING

Definition

The system of sets $S_1,\ S_2, \ldots$ is said to form a packing into the set S, if

$$S_i \cap S_j = \emptyset \ (i \neq j)$$
$$\bigcup_i S_i \subset S$$

i.e if no two of the sets $S_1,\ S_2, \ldots$ have any element in common and each element of the sets $S_1,\ S_2, \ldots$ belongs to S.

Definition

Let $\mathbf{a_1}, \mathbf{a_2}, \ldots, \mathbf{a_n}$ be n linearly independent vectors in $\mathbf{E}^n$. The set $\Lambda = \{u_1\mathbf{a_1} + u_2\mathbf{a_2} + \cdots + u_n\mathbf{a_n} \mid u_i \in \mathbb{Z}\}$ is called a **lattice** and $\overline{\Lambda} = \{v_1\mathbf{a_1} + v_2\mathbf{a_2} + \cdots + v_n\mathbf{a_n} \mid v_i \in [0, 1]\}$ is called a **unit cell**.

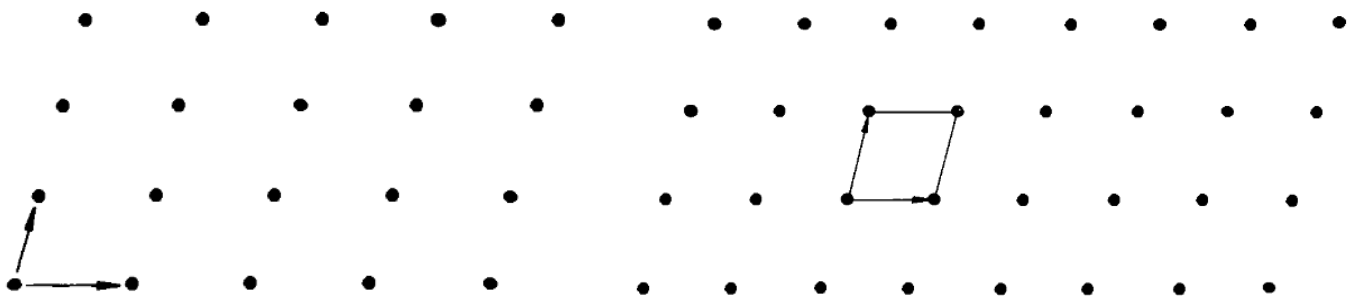


Figure: (a) A plane lattice and (b) a corresponding unit cell.

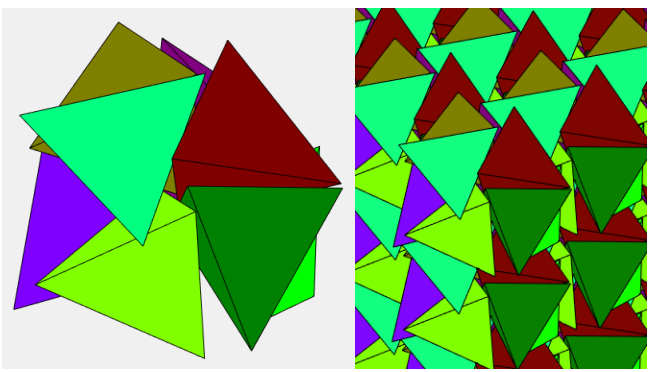
Definition

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.

- $\mathbf{a_1}, \mathbf{a_2}, \ldots, \mathbf{a_N} \in \overline{\Lambda}$
- $\mathbf{b_1}, \mathbf{b_2}, \ldots \in \Lambda$
- $R_1, R_2, \ldots, R_N \in SO(n) = \{A \in \mathbb{R}^{n \times n} : A^T A = I,\ \det A = 1\}$.



(a) (b)

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

Definition

The periodic packing density $\rho(\mathcal{K}_P)$ of the periodic packing $\mathcal{K}_P$ is

$$\rho(\mathcal{K}_P) = \frac{N\mathtt{vol}(K)}{|\det(\Lambda)|}.$$

Periodic packing problem statement:

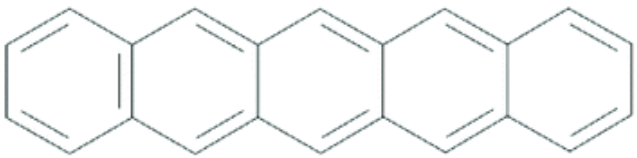
$$\mathcal{K}_{\max} = \operatorname*{argmax}_{\mathcal{K}_P} \rho(\mathcal{K}_P).$$

PRELIMINARY RESULTS

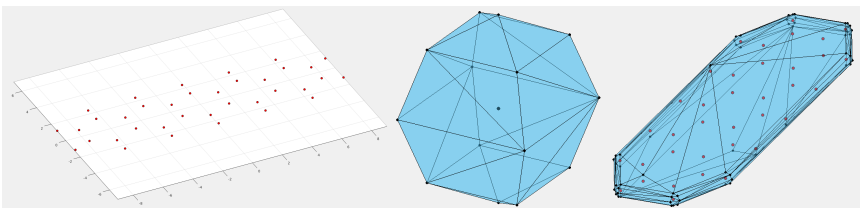
Preliminary results

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)



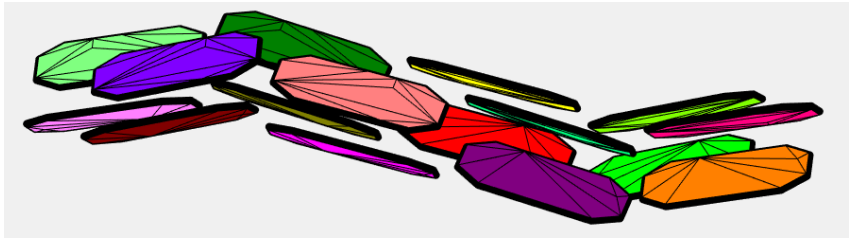
(b) (c) (d)

Figure: (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).

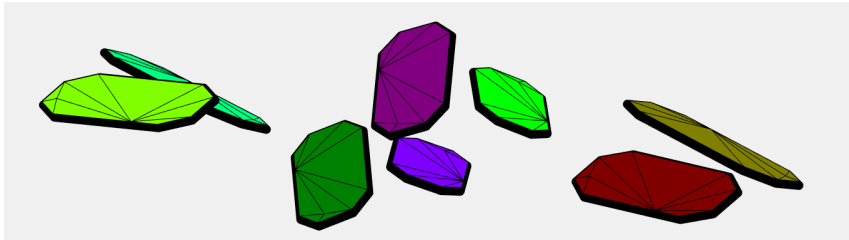
Preliminary results

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)

Figure: (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

- Implemented the Torquato-Jiao packing algorithm[1] in Julia programming language with a modification in the unit cell adaptation acceptance rate:

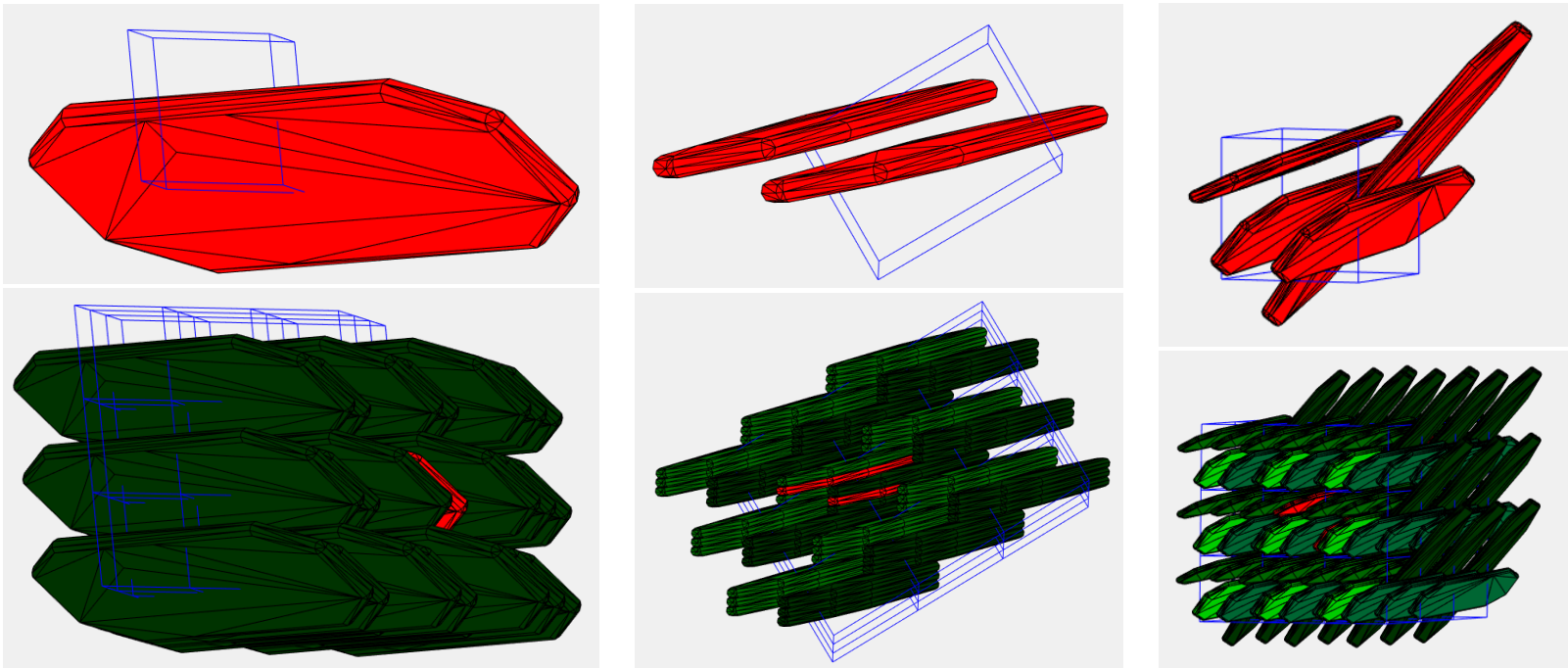
$$P(\mathcal{K}_t \leftarrow \mathcal{K}_{new}) = \begin{cases} 1 & \text{if } \Delta\rho > 0 \\ e^{\frac{-\Delta\rho}{T_t}} & \text{if } \Delta\rho \leq 0 \end{cases}$$

  where $\Delta\rho = \rho(\mathcal{K}_{new}) - \rho(\mathcal{K}_t)$.
- Used the algorithm to find dense periodic packings of the pentacene model

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

Preliminary results

Pentacene packings

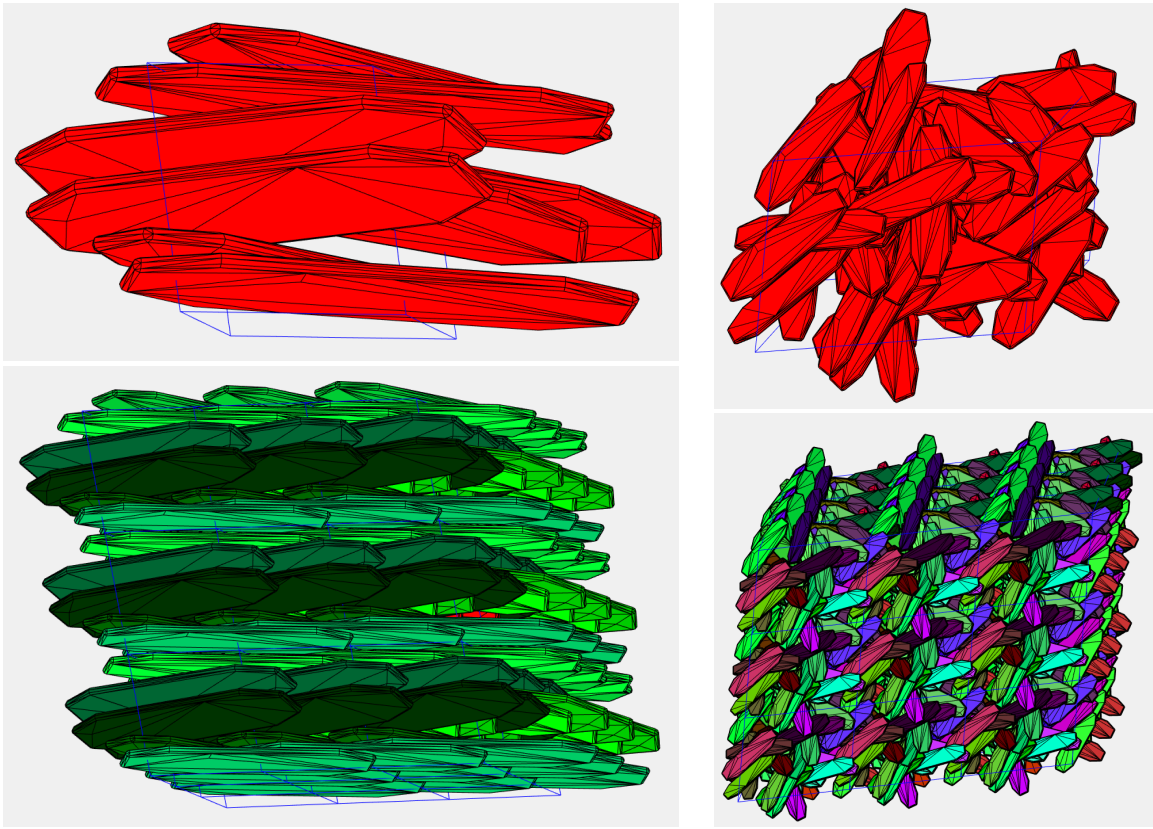


(a) (b) (c)

Figure: Densities of packings of (a) 1 $\rho \approx 1$, (b) 2 $\rho \approx 1$, (c) 4 $\rho = 0.8093$ pentacene models.

Preliminary results

Pentacene packings



(a) (b)

Figure: Densities of packings of (a) 8 $\rho = 0.6940$ and (b) 54 $\rho = 0.1521$ pentacene models.

Problem statement:

$$\min \mathtt{obj} = \min \mathtt{vol}(\overline{\Lambda}) = \min \det(\Lambda)$$

as a function of $4 + 3N$ variables i.e $\mathtt{obj}(\mathbf{u}_1, \mathbf{u}_2, \mathbf{c}_1, \ldots, \mathbf{c}_N, \theta_1, \ldots, \theta_N)$, subject to

$$\mathbf{c}_k, \mathbf{c}_l \in \overline{\Lambda}$$

$$\mathtt{Int}(T_k) \cap \mathtt{Int}(T_l^{i,j}) = \emptyset$$

for $k, l = 1, 2, \ldots, N$, $i, j = -2, -1, 0, 1, 2$, excluding the case when $l = k, i = 0, j = 0$.

- $\mathtt{Int}(\cdot)$ is the interior of a set.
- $\mathbf{c}_k$ is the centre of 2-simplex T_k.
- $T_l^{i,j}$ is a copy of 2-simplex T_l in the unit cell (i, j).

Preliminary results

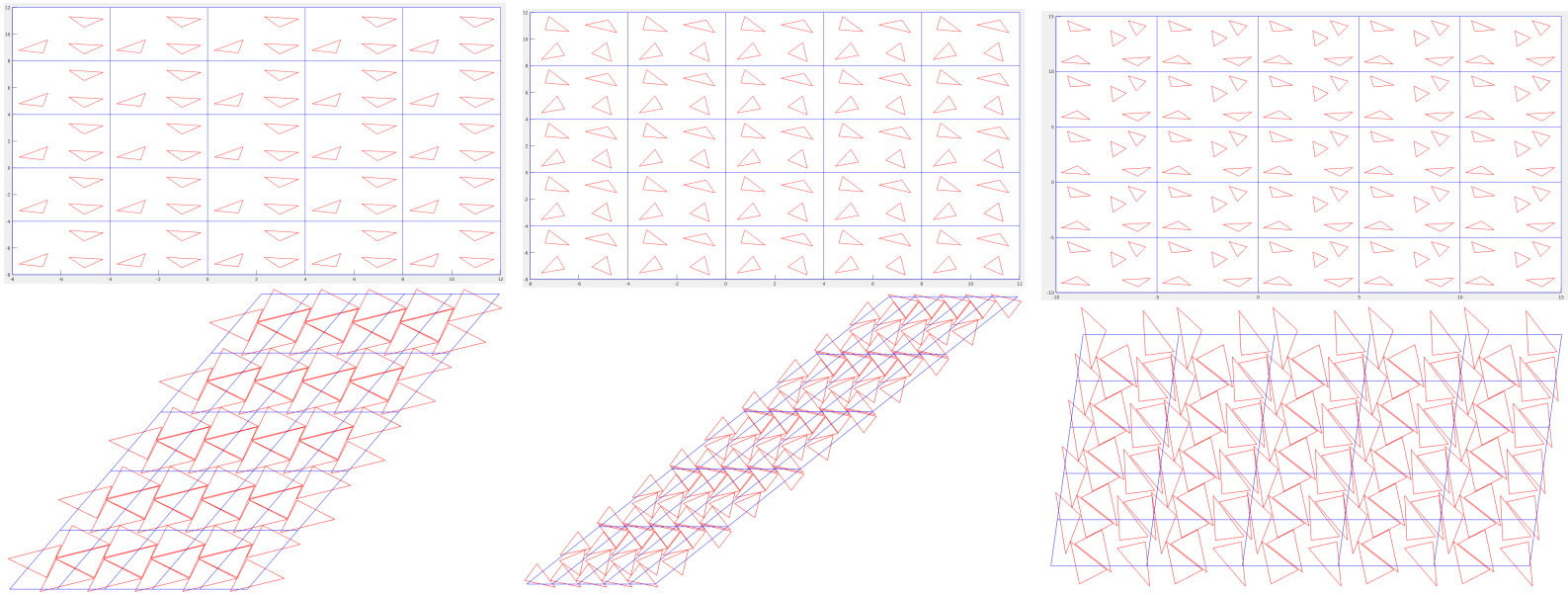
Experiments: Nonlinear constrained optimization

- Used Matlab's optimization toolbox nonlinear constrained solver to find dense packings of 2, 3, 4, 5 simplexes in a unit cell.
- 100 runs with random initial configurations (rotations) for each setting.
- Results:
  Setting with 2 simplexes generated optimal solutions but with degenerate unit cells i.e $\det(\Lambda) \approx 0$.

Setting	Feasible solutions found	$\bar{\rho}$	$\mathtt{Var}(\rho)$	$\max \rho$
3	39	0.5827	0.0197	0.8118
4	20	0.5850	0.0127	0.7959
5	9	0.5637	0.0111	0.7246

Preliminary results

Experiments: Nonlinear constrained optimization



(a) (b) (c)

Figure: Best solutions found using nonlinear constrained optimization for (a) 3, (b) 4, (c) 5 simplexes in a unit cell. For each case initial (upper image) and output (lower image) configurations are displayed.

FUTURE WORK

Future work

Limitations of presented methods

1. Modelling

- Pentacene has 4 main packing types.
- Monte-Carlo packing algorithm $\rightarrow \beta$

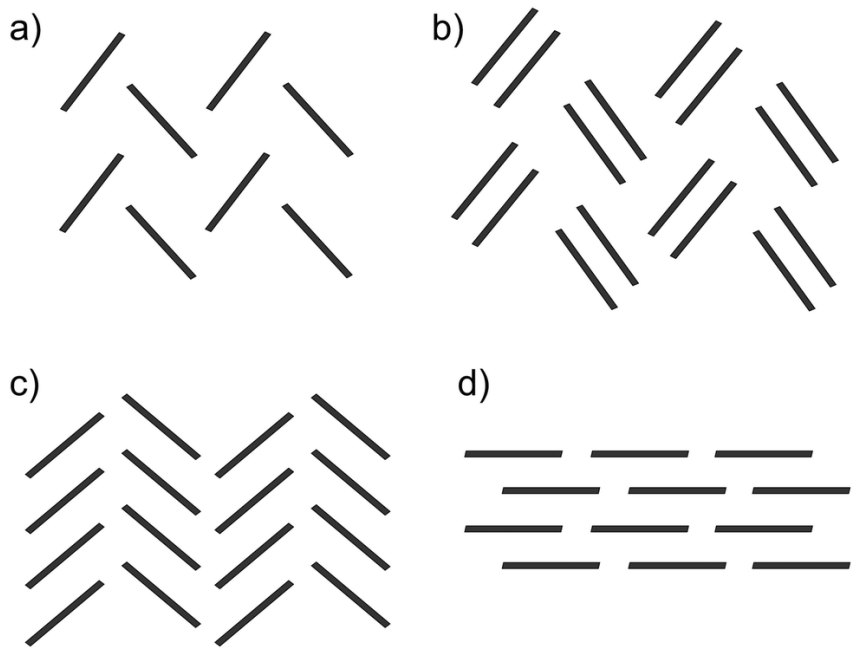


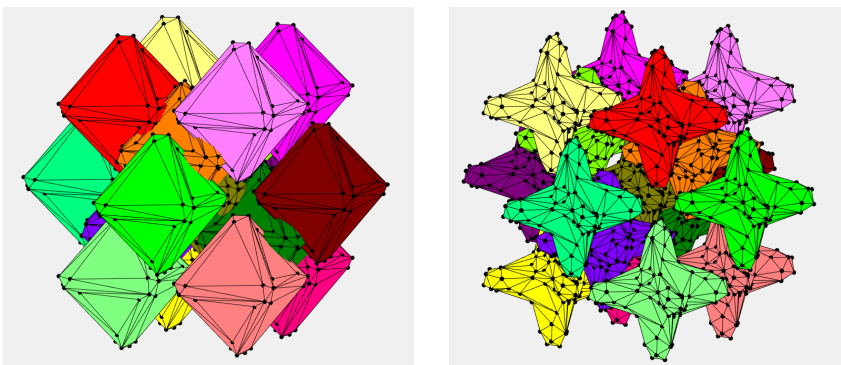
Figure: (a) herringbone; (b) sandwich herringbone; (c) γ and (d) sheet (β).

2. Optimization methods

- Decreasing packing density with increasing number of objects in the unit cell.
- Solutions depend on initial configurations.
- Complicated configuration space $\rightarrow$ Complicated objective function landscape (many hills and valleys) $\rightarrow$ Hill climbing is necessary.

3. Concavity

- 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.



(a) (b)

Figure: (a) convex hull and (b) α-shape of an organic cage molecule crystal structure.

1. Modelling

- Make use of space-groups
- Adjust only one object in the unit cell and the unit cell itself. The rest is given by space-group symmetries (230).

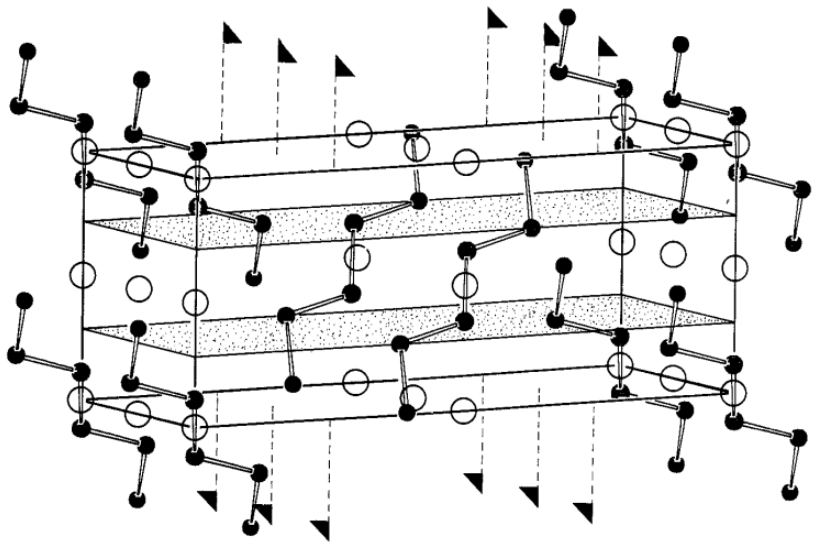


Figure: A $P2_1/c$ crystal structure and its symmetry elements with. Glide planes are emphasized by the shading.

2. **Optimisation methods**
   - Explore black box optimisation methods and replace the Simulated annealing schedule
     - Evolution strategies
       - Covariance matrix adaptation evolution strategy
       - Natural evolution strategy
3. **Concavity**
   - Implement overlap checks for concave polyhedra.
     - Convex decomposition

THANK YOU

APPENDIX

Packing extended

Definition

The density $\rho(\mathcal{K})$ of the packing $\mathcal{K}$ is

$$\rho(\mathcal{K}) = \limsup_{c \to \infty} \rho(\mathcal{K}, C)$$

where

$$\rho(\mathcal{K}, C) = \frac{1}{\mathtt{vol}(C)} \sum_{(R_j K + a_i) \cap C \neq \emptyset} \mathtt{vol}(R_j K + a_i).$$

- $\{a_i\}$ be a sequence of points.
- $\{R_j : R_j \in SO(3)\}$ a collection of rotations.
- K a set with finite volume $\mathtt{vol}(K)$.
- C a cube with the edge length c.
- $\mathcal{K} = \{R_j K + a_i\}$ a system of sets that forms a packing.
- If $\rho(\mathcal{K})$ is a packing then $0 \leq \rho(\mathcal{K}) \leq 1$.

Theorem

Let K be a bounded set with positive measure, let C be a cube (with its edges parallel to the coordinate axes) with edge-length $s(C)$, and let T be a non-singular affine transformation. Let $\mathbf{a_1}, \mathbf{a_2}, \ldots, \mathbf{a_N}$ be a set of points, and let $\mathbf{b_1}, \mathbf{b_2}, \ldots$ be the points of the lattice of all points that have integral multiples of $s(C)$ for co-ordinates. Let $\mathcal{K}_P$ be the periodic system of sets

$$K + \mathbf{a_i} + \mathbf{b_j} \ \ (i = 1, 2, \ldots, N;\ j = 1, 2, \ldots)$$

and let $T\mathcal{K}_P$ denote the system of sets

$$T\left(K + \mathbf{a_i} + \mathbf{b_j}\right) \ \ (i = 1, 2, \ldots, N;\ j = 1, 2, \ldots).$$

Then

$$\rho\left(T\mathcal{K}_P\right) = \rho\left(\mathcal{K}_P\right) = \frac{N\mathtt{vol}(K)}{\mathtt{vol}(C)}.$$

Packing extended

Bodies K for which the densest packing is known

BODY	SOURCE
Circular disk in $\mathbb{E}^2$	[Thu10]
Parallel body of a rectangle	[Fej67]
Intersection of two congruent circular disks	[Fej71]
Centrally symmetric n-gon (algorithm in $O(n)$ time)	[MS90]
Ball in $\mathbb{E}^3$	[Hal05]
Ball in $\mathbb{E}^8$	[Via17]
Ball in $\mathbb{E}^{24}$	[CKM17]
Truncated rhombic dodecahedron in $\mathbb{E}^3$	[Bez94]

Packing extended

Bodies K $\in$ $\mathbf{E}^3$ for which the densest lattice packing is known

BODY	$\delta_L(K)$	SOURCE
$\{x \mid \lvert x\rvert \le 1,\ \lvert x_3\rvert \le \lambda\} \quad (\lambda \le 1)$	$\pi(3-\lambda^2)^{1/2}/6$	[Cha50]
$\{x \mid \lvert x_i\rvert \le 1,\ \lvert x_1+x_2+x_3\rvert \le \lambda\}$	$\frac{9-\lambda^2}{9}$ for $0<\lambda\le\frac{1}{2}$; $\frac{9\lambda(9-\lambda^2)}{4(-\lambda^3-3\lambda^2+24\lambda-1)}$ for $\frac{1}{2}\le\lambda\le 1$; $\frac{9(\lambda^3-9\lambda^2+27\lambda-3)}{8\lambda(\lambda^2-9\lambda+27)}$ for $1\le\lambda\le 3$	[Whi51]
$\{x \mid \sqrt{(x_1)^2+(x_2)^2}+\lvert x_3\rvert \le 1\}$	$\pi\sqrt{6}/9 = 0.8550332\ldots$	[Whi48]
Tetrahedron	$18/49 = 0.3673469\ldots$	[Hoy70]
Octahedron	$18/19 = 0.9473684\ldots$	[Min04]
Dodecahedron	$(5+\sqrt{5})/8 = 0.9045084\ldots$	[BH00]
Icosahedron	$0.8363574\ldots$	[BH00]
Cuboctahedron	$45/49 = 0.9183633\ldots$	[BH00]
Icosidodecahedron	$(45+17\sqrt{5})/96 = 0.8647203\ldots$	[BH00]
Rhombic Cuboctahedron	$(16\sqrt{2}-20)/3 = 0.8758056\ldots$	[BH00]
Rhombic Icosidodecahedron	$(768\sqrt{5}-1290)/531 = 0.8047084\ldots$	[BH00]
Truncated Cube	$9(5-3\sqrt{2})/7 = 0.9737476\ldots$	[BH00]
Truncated Dodecahedron	$(25+37\sqrt{5})/120 = 0.8977876\ldots$	[BH00]
Truncated Icosahedron	$0.78498777\ldots$	[BH00]
Truncated Cuboctahedron	$0.8493732\ldots$	[BH00]
Truncated Icosidodecahedron	$(19+10\sqrt{5})/50 = 0.8272135\ldots$	[BH00]
Truncated Tetrahedron	$207/304 = 0.6809210\ldots$	[BH00]
Snub Cube	$0.787699\ldots$	[BH00]
Snub Dodecahedron	$0.7886401\ldots$	[BH00]

Preliminary results extended

Preliminary results extended

Torquato and Jiao 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 successful rotation/translation 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.

Restrictions:

- Only the centres of the packed objects have to be contained inside the unit cell.
- No overlaps between the objects in the unit cell and neighbouring unit cells.

Theorem

Two convex polyhedra do not intersect if and only if there exists a separating plane which is either parallel to a face of one polyhedron or which is parallel to at least one edge of each polyhedron.

- A consequence of Minkowsky's *Separating hyperplane theorem*
- A and B do not overlap $\Leftrightarrow$ orthogonal projections of A and B onto the normal of the separating hyperplane (separating axis) do not overlap.
- For two general polyhedrons with the same number of faces (F) and edges (E) there are $2F + E^2$ potential separating axes.
- Limits the overlap check only to convex sets.

The model:

- $\Lambda = \left\{ p_1 u_1 + p_2 u_2 \mid p_1, p_2 \in [0,1]; u_1, u_2 \in \mathbb{R}^2 \right\}$ a unit cell defined by the set of generators $\overline{\Lambda} = \begin{pmatrix} u_{11} & u_{12} \\ u_{21} & u_{22} \end{pmatrix}$
- $T_0 = \left\{ \phi_1 \binom{1}{0} + \phi_2 \binom{0}{1} - \binom{\frac{1}{3}}{\frac{1}{3}} \mid 0 \leq \phi_1 + \phi_2 \leq 1 \right\}$ a 2-simplex centred at the origin.

The model (continued):

- N copies of T_0 translated by $c_k \in \mathbb{R}^2$ and rotated by $R_k \in SO(2)$:

$$T_k = \left\{ \overline{\Lambda} c_k + R_k p_0 \mid p_0 \in T_0 \right\}$$

where $c_k = \begin{pmatrix} x^k \\ y^k \end{pmatrix} \in [0,1] \times [0,1]$ and $R_k = \begin{pmatrix} \cos\theta_k & -\sin\theta_k \\ \sin\theta_k & \cos\theta_k \end{pmatrix}$ for $k = 1, 2, \ldots, N$ and $\theta_k \in [0, 2\pi]$.

- Translates $T_k^{i,j}$ of T_k in the neighbouring unit cells

$$T_k^{i,j} = \left\{ \overline{\Lambda} \begin{pmatrix} i \\ j \end{pmatrix} + p_k \mid p_k \in T_k \right\}$$

for $i, j \in \{-2, -1, 0, 1, 2\}$.

Preliminary results extended

Alternative constrains formulation

- Define separating hyperplanes by

$$\alpha_h x + \beta_h y + \gamma_h = 0$$

for $h = 1, 2, 3$ where $\alpha_h, \beta_h, \gamma_h$ are given by the edges of T_0.

- Vertices of T_0:

$$\begin{pmatrix} x_0 \\ y_0 \end{pmatrix} \in \texttt{Vert}(T_0)$$

.

- Vertices of T_k:

$$\begin{pmatrix} x_k^{0,0} \\ y_k^{0,0} \end{pmatrix} = \overline{\Lambda} c_k + R_k \begin{pmatrix} x_0 \\ y_0 \end{pmatrix} \in \texttt{Vert}(T_k)$$

- Vertices of $T_l^{i,j}$:

$$\begin{pmatrix} x_l^{i,j} \\ y_l^{i,j} \end{pmatrix} = \overline{\Lambda} \left(c_l + \begin{pmatrix} i \\ j \end{pmatrix} \right) + R_l \begin{pmatrix} x_0 \\ y_0 \end{pmatrix} \in \texttt{Vert}(T_l^{i,j})$$

Preliminary results extended

Alternative constrains formulation

- Vertices of T_k in the coordinate system of $T_l^{i,j}$:

$$\begin{pmatrix} \tilde{x}_k^{0,0} \\ \tilde{y}_k^{0,0} \end{pmatrix} = R_l^{-1} \left[\begin{pmatrix} x_k^{0,0} \\ y_k^{0,0} \end{pmatrix} - \overline{\Lambda} \left(c_l + \begin{pmatrix} i \\ j \end{pmatrix} \right) \right]$$

- Vertices of $T_l^{i,j}$ in the coordinate system of T_k:

$$\begin{pmatrix} \tilde{x}_l^{i,j} \\ \tilde{y}_l^{i,j} \end{pmatrix} = R_k^{-1} \left[\begin{pmatrix} x_l^{i,j} \\ y_l^{i,j} \end{pmatrix} - \overline{\Lambda} c_k \right].$$

Preliminary results extended

Alternative constrains formulation

$$\mathtt{Int}(T_k) \cap \mathtt{Int}(T_l^{i,j}) = \emptyset$$

$$\Leftrightarrow \min_{i,j,k,l} \max\{ \max_{1\leq h\leq 3} \min_{\binom{x_0}{y_0}\in \mathtt{Vert}(T_0)} v_{h,k}^{0,0}, \max_{1\leq h\leq 3} \min_{\binom{x_0}{y_0}\in \mathtt{Vert}(T_0)} v_{h,l}^{i,j}\} \geq 0$$

where

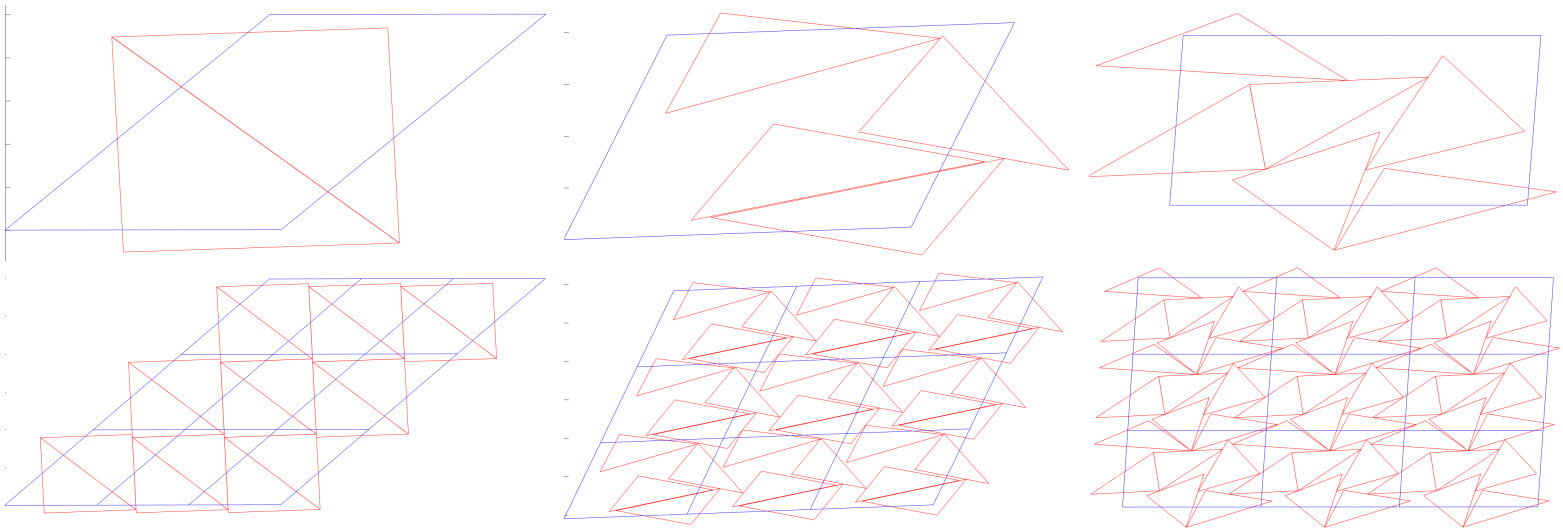
$$v_{h,k}^{0,0} = \alpha_h \tilde{x}_k^{0,0} + \beta_h \tilde{y}_k^{0,0} + \gamma_h$$
$$v_{h,l}^{i,j} = \alpha_h \tilde{x}_l^{i,j} + \beta_h \tilde{y}_l^{i,j} + \gamma_h$$

,$\alpha_h, \beta_h, \gamma_h$ are the coefficients of the separating hyperplanes of T_0 defined in previously and $k, l = 1, 2, \ldots, N$, $i, j = -2, -1, 0, 1, 2$, excluding the case when $l = k, i = 0, j = 0$.

Preliminary results extended

Experiments: Genetic algorithm

- Tested using Matlab's Global optimization toolbox genetic algorithm.



(a) (b) (c)

Figure: Output configurations of genetic algorithm for the packing of (a) 2 $\rho = 1$, (b) 4 $\rho = 0.6715$, (c) 6 simplexes $\rho = 0.7534$ in a unit cell.