Energy and Entropy, Cluster Models

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Energy and Entropy

Relevant for thermodynamical stability is free energy $F = U - TS$.

Important energy contributions:

- local energies
- Hume-Rothery mechanism (non-local)

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Important energy contributions:

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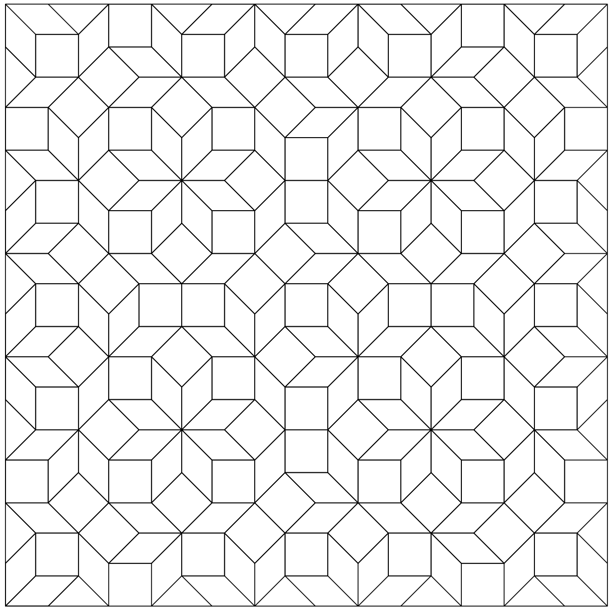
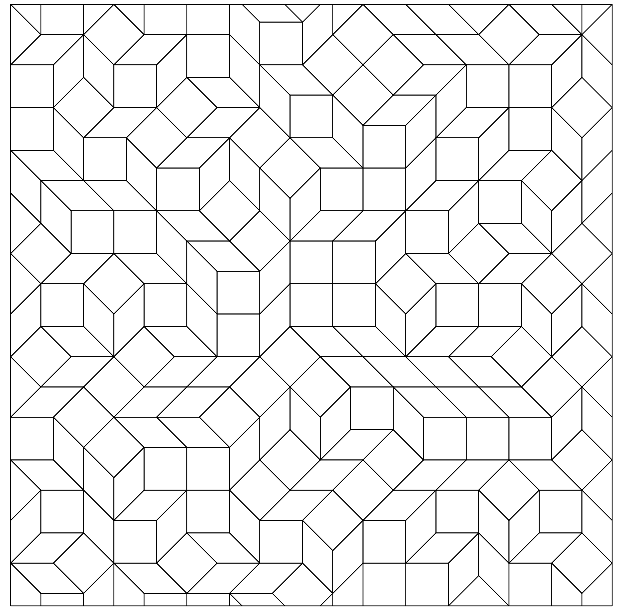
Important entropy contributions:

- (partial) chemical disorder
- vacancies
- configurational entropy (random tilings)

Ordered and Random Tilings





Ordered tiling: number of R-patches $N(R)$ grows algebraically.
Random tiling: number of R-patches $N(R)$ grows exponentially.
Positive entropy density:

$$\sigma = \lim_{R\to\infty} \frac{1}{V_R} k_B \ln N_R > 0$$

Random Tilings

Properties:

- typical RT are homogeneous
- lift to lattice follows a plane
- entropy maximum at highest symmetry
- entropy varies quadratically as function slope (or tile densities)

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Methods:

- transfer matrix
- some examples in 2D exactly soluble (Bethe ansatz)
- Monte Carlo simulation with periodic or open boundaries
- entropy determination with entropic sampling

Entropy Orders at High Temperature

Entropic elastic energy:

$$\int d^3x\, \partial_i h_j C_{ij\ell m} \partial_\ell h_m$$

Correlation function: for $|x| \to \infty$ we have

$$\langle (h_i(x) - h_i(0))(h_j(x) - h_j(0)) \rangle \leq const \quad (3D)$$
$$\langle (h_i(x) - h_i(0))(h_j(x) - h_j(0)) \rangle \sim \ln |x| \quad (2D)$$

Bragg peaks for 3D Random Tiling!

Energy Orders at Low Temperature

Local energies prefer certain tiles and tile configurations
$\longrightarrow$ Cluster Models.

At high temperature, energy differences between tile configurations unimportant $\longrightarrow$ Random Tiling

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Possible phase transition between perfect and random tiling state.

Perfect state can be quasicrystalline or crystalline.

2D quasicrystals are always in Random Tiling phase (Kalugin 1989).

Experimental Evidence for Random Tilings

Direct observation in electron microscope (decagonal quasicrystals).

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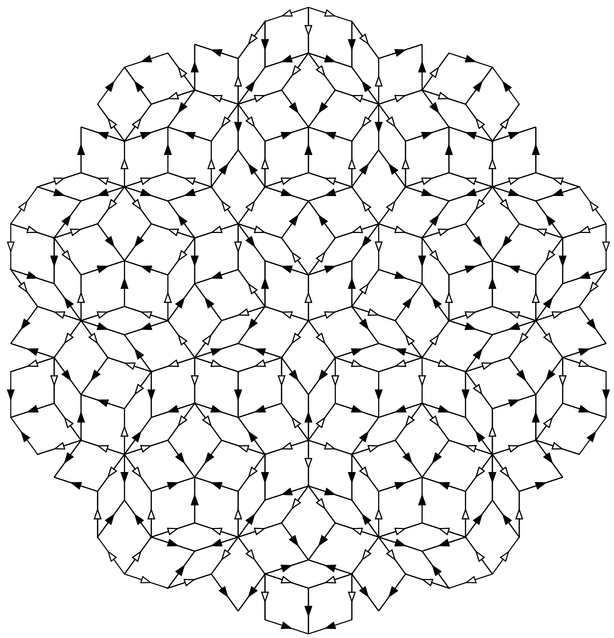
Above 700K transition to plastic behaviour. Depinning of phasons?

Energy Based on Matching Rules?



Idea: prefer all allowed patches, punish all disallowed ones...
Gets hopelessly complex!

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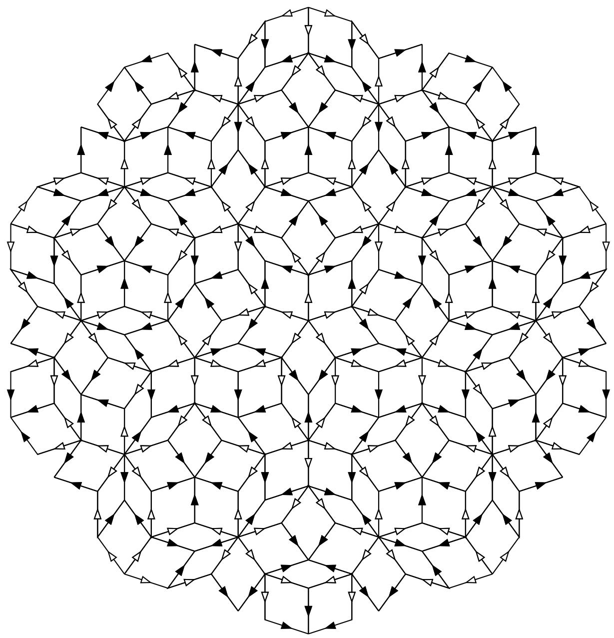

Idea: prefer all allowed patches, punish all disallowed ones...
Gets hopelessly complex!

However, not all patches are equally important. Some cover even the whole structure, with overlaps.

Overlaps produce constraints, which can lead to order.

Cluster Models

Characteristic clusters may cover the whole structure. These must be preferred.

Order principles:

- maximize cluster denstity.
- require, that cluster covers the structure
- maximal cluster covering

Cluster overlaps lead to correlations and order.

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Two cases:

- overlap rules generate ordered structure: energetic stabilisation
- overlap rules generate only local order: entropic stabilisation

Cluster Maximization

First proposed by Jeong and Steinhardt (Phys. Rev. Lett, 1994).

Preferring few, well-selected clusters generates Penrose tiling.

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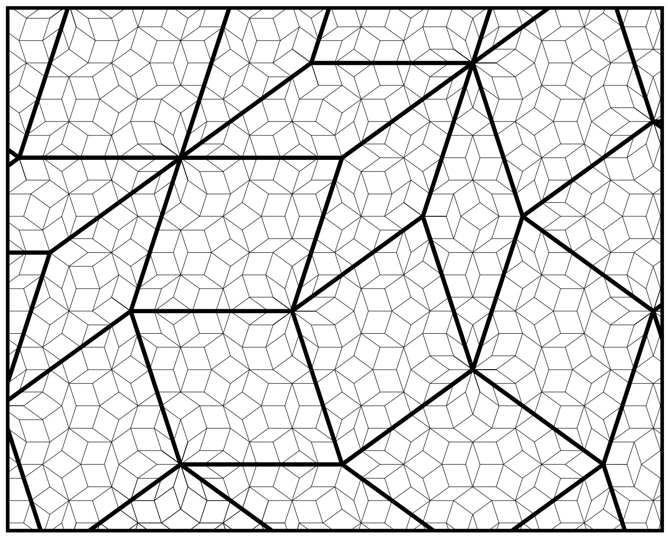
Finding such clusters is not easy: typically, one gets a supertile random tiling:



Ground state is periodic approximant.

At higher temperature: supertile random tiling, ordered locally, disordered at larger scales.

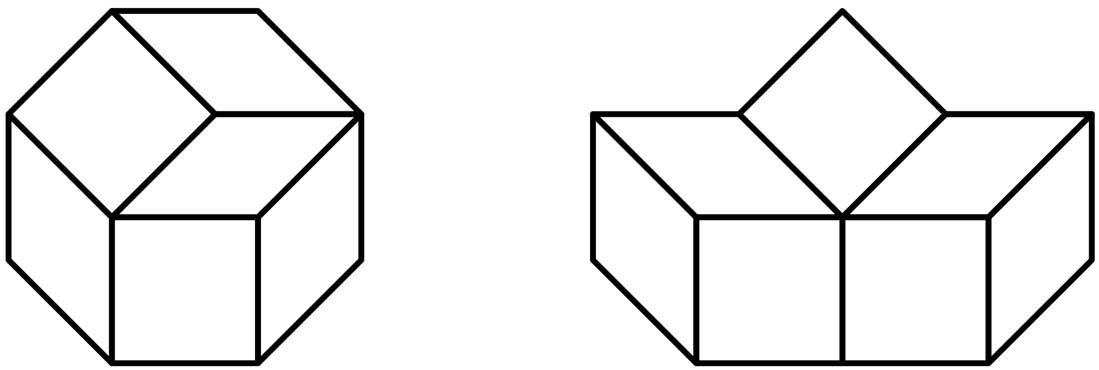
Cluster density maximization efficient concept;
no need to consider all local configurations.

Range of interaction can not be reduced, however.

Example for Energetic Stabilization

Square-rhombus tilings satisfying the alternation condition are quasiperiodic and 4-fold symmetric (A. Katz, 1995).

These clusters favour alternation condition:



Maximizing Cluster Density

If alternation condition is satisfied: compute cluster densities analytically!

Octagonal tiling has highest cluster density, provided

$$(1+\sqrt{2}) < \frac{2E_{oct}}{E_{ship}} < (1+\sqrt{2})^5$$

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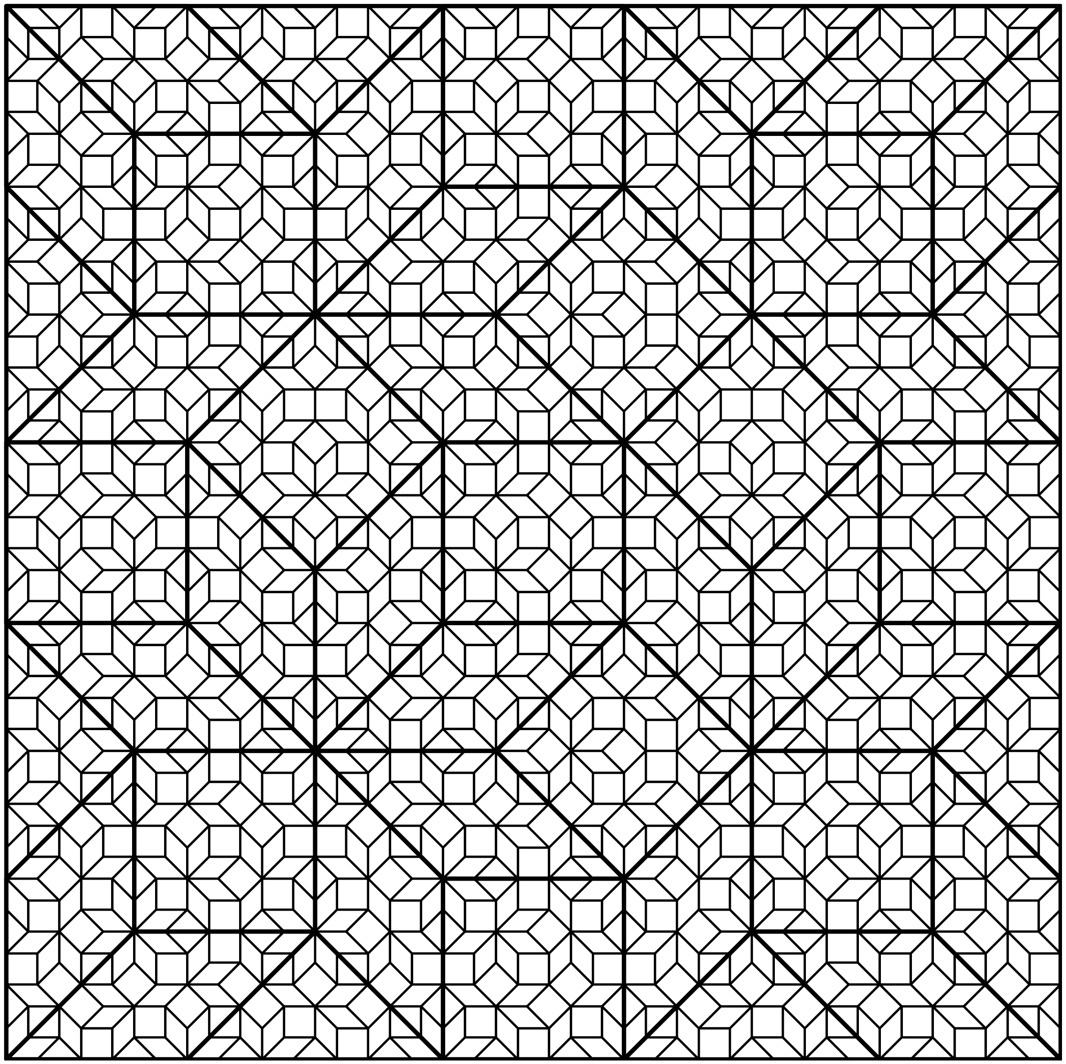
Monte-Carlo simulations: octagonal has highest cluster density among all tilings (F.G., H.-C. Jeong, J. Phys. A, 1995).

Octagonal tiling is ground state of simple cluster model (two clusters), even though it admits no perfect matching rules.

Get Away With One Cluster?



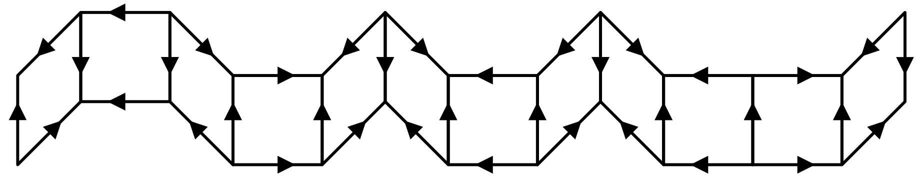
Maximizing octagon alone does not work.

At fixed stoichiometry, all supertile random tilings have same octagon density.

Octagon density maximal for periodic approximant.

Decorated Cluster

Alternation condition enforced by arrows:



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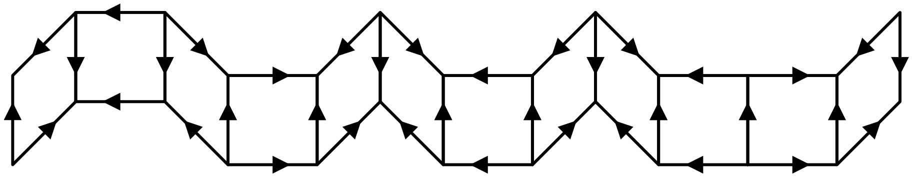
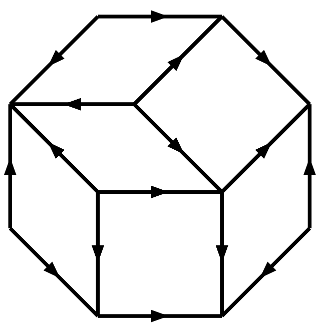
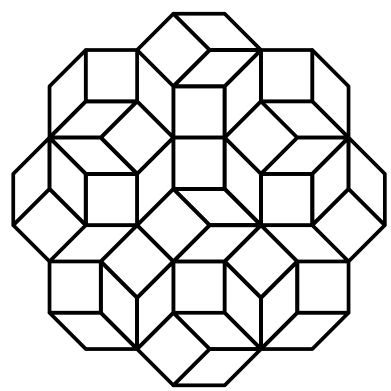


Idea: take arrowed octagon cluster!





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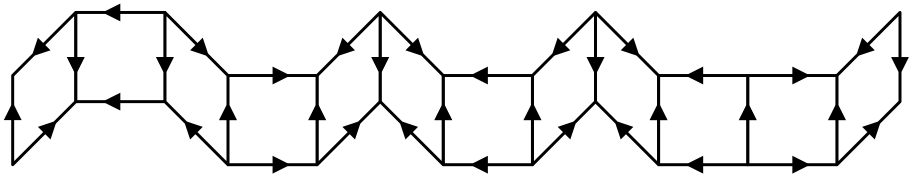

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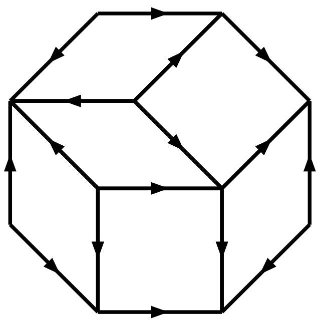
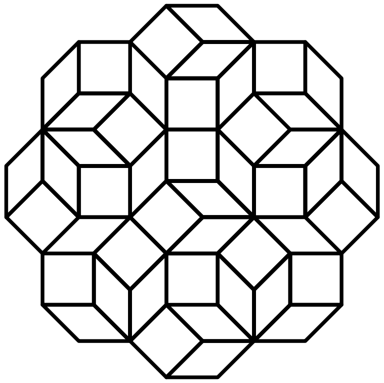


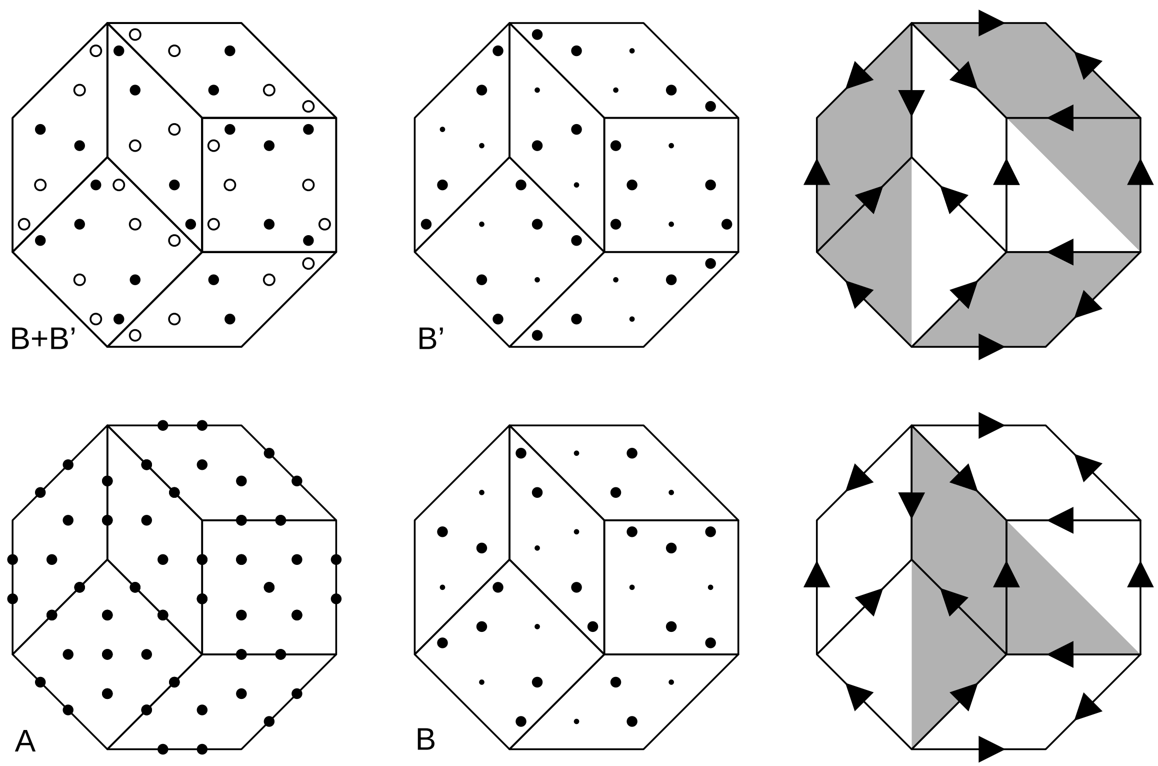


A tiling covered by arrowed octagon satisfies alternation condition.

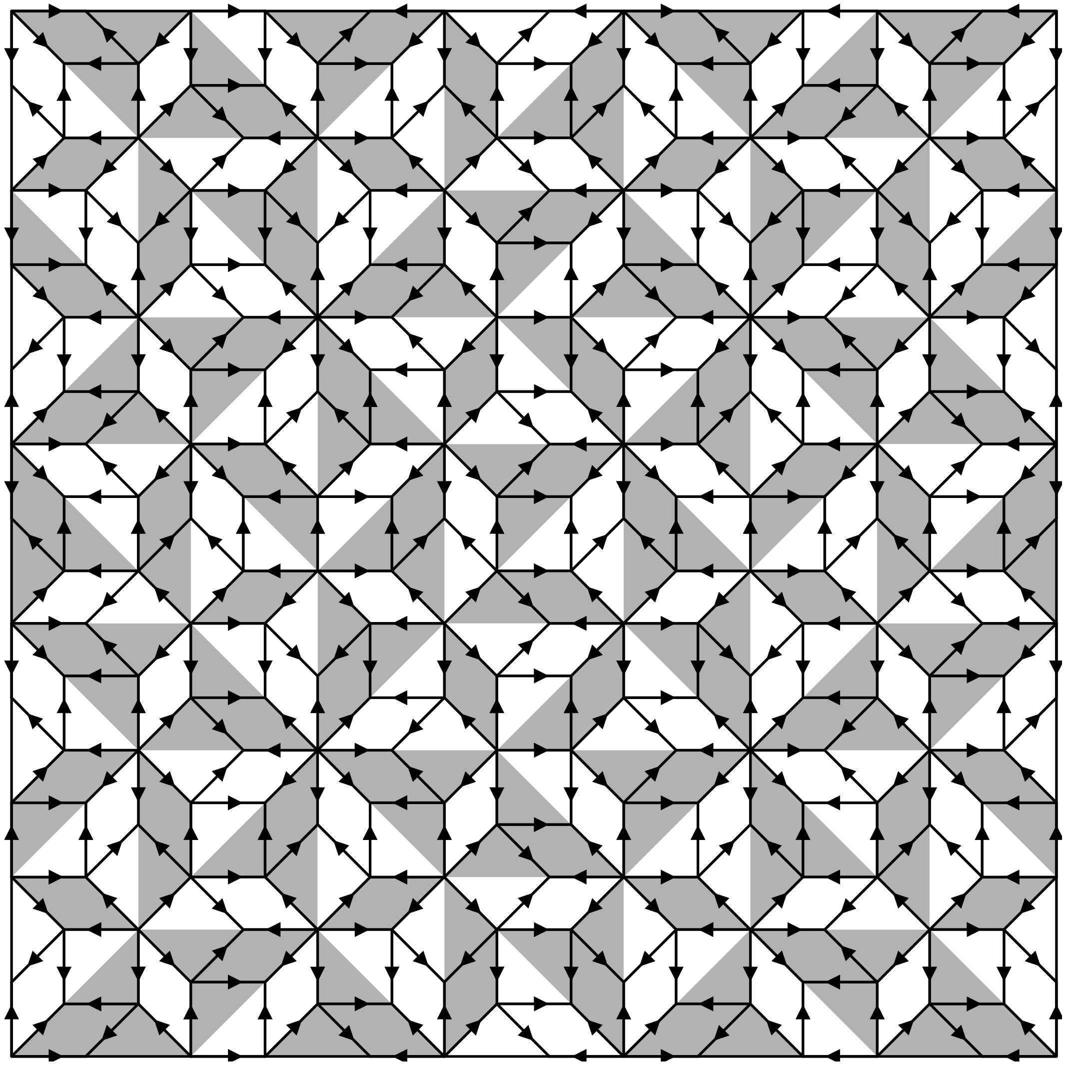
Octagonal tiling has highest cluster density.

Atomistic Model

Model for octagonal AlMnSi;
Experiment: Jiang, Hovmöller and Zhou (Phil. Mag. Lett. 1995),
Theory: S.I. Ben-Abraham and F.G. (Phys. Rev. B, 1999) Stacking
$\ldots ABAB' \ldots$



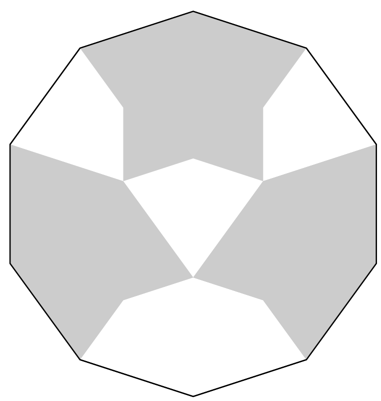
Covering with Colored Octagon

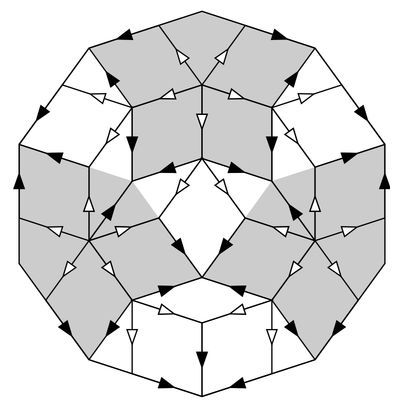


Gummelt's Aperiodic Decagon

P. Gummelt (1995, 1996): each covering of the plane with the aperiodic decagon is equivalent to a Penrose tiling (and vice versa).

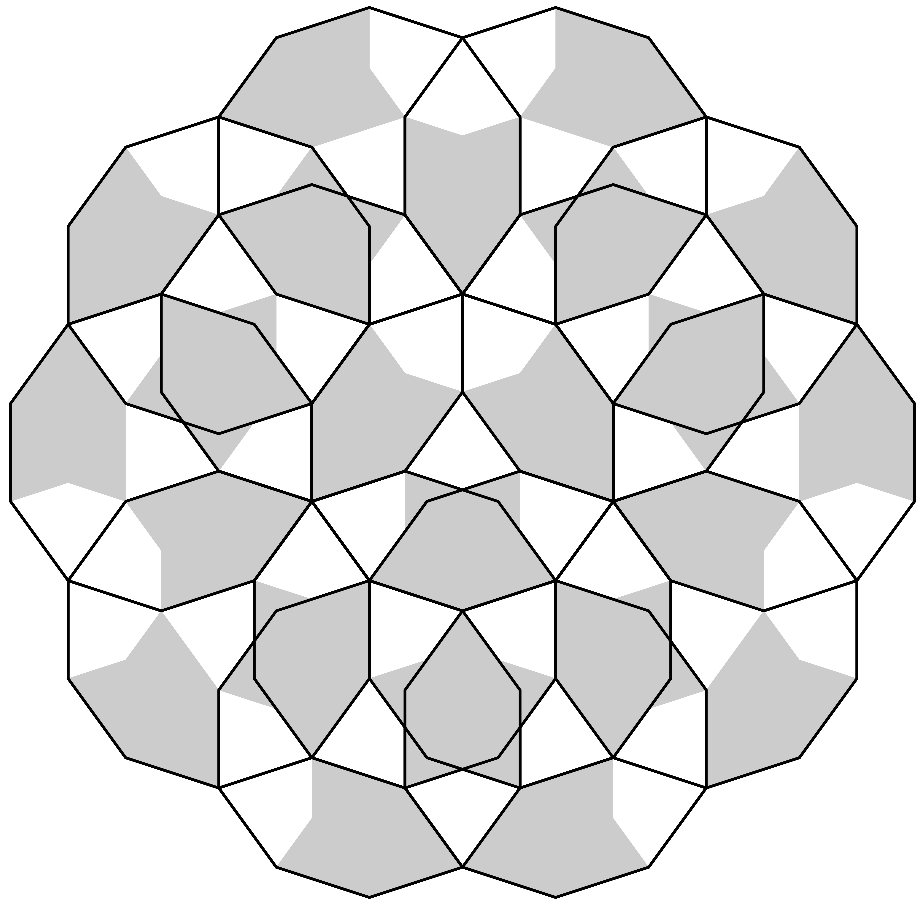
Coverings and Penrose tilings are MLD.





In the overlap, colors must match.

Jeong and Steinhardt (Phys. Rev. B, 1997): Coverings have highest cluster density.



Many authors have constructed atomic models based on Gummelt's decagon, such that the atomic decoration enforces equivalent (or similar) overlap rules.

arrows, respectively. In type B overlap, beside the four Al column pairs (indicated by the white arrows), there are

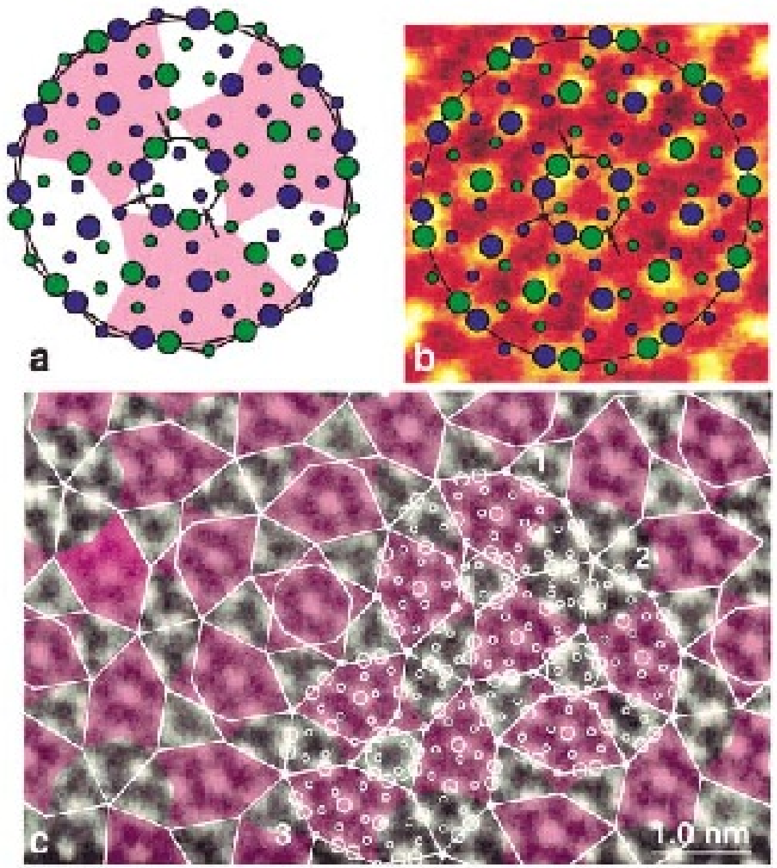


FIG. 3 (color). (a) Structure with chemical ordering and broken symmetry after total energy relaxation. The three arrows indicate the three Al columns that moved towards the center. The broken symmetry is represented by the pink subtiles. (b) The relaxed structure superimposed on a Z-contrast image. (c) A Z-contrast image with lower magnification showing more 2 nm clusters. The layout shows the overlaps of 2 nm clusters, giving the same tiling as the Gummelt coverage model.

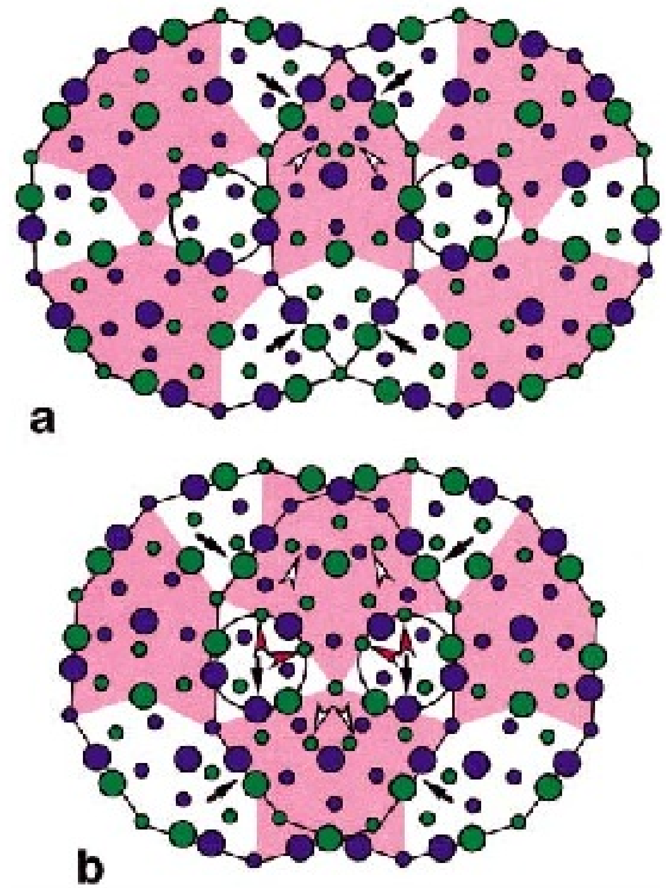
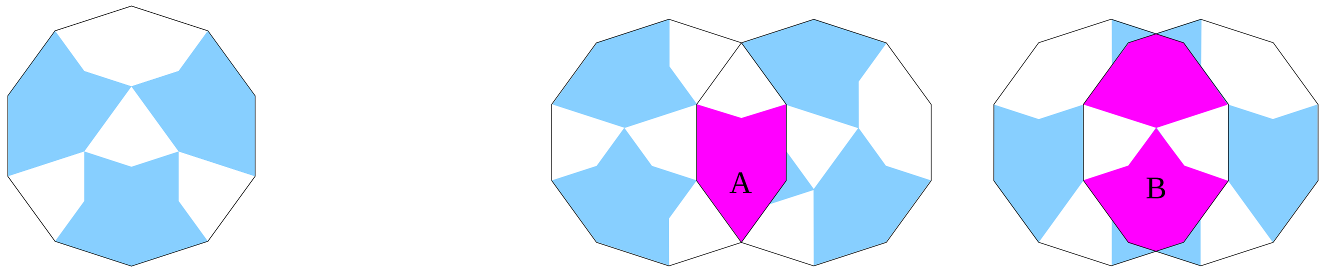


FIG. 4 (color). The details of the (a) type A and (b) type B overlaps.

Yan and Pennycook, Phys. Rev. Lett. **86**, 1542 (2001).

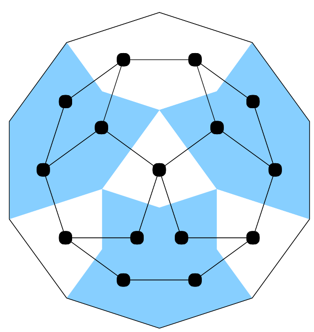
Example of Entropy Stabilisation

Relax Gummelt's overlap rules:

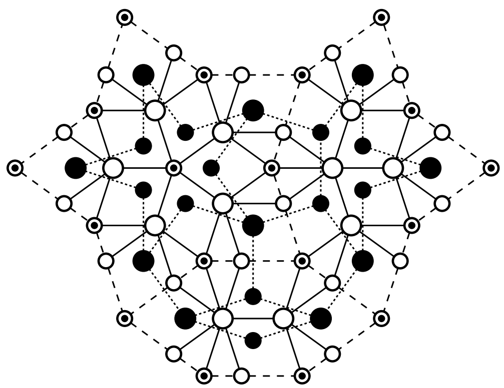


Relaxed Overlap-Rules: Perfect B-overlaps, unoriented A-overlaps.

Realisation:



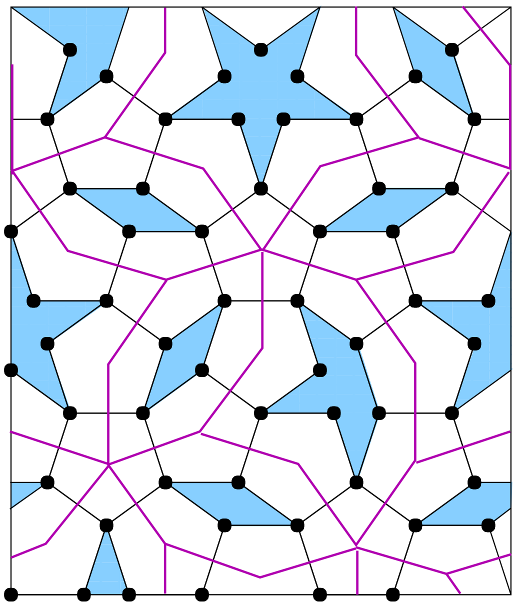
Vertex-Cluster



Roth-Henley

Properties of Relaxed Coverings

- Decagon centers are vertices of random Penrose Pentagon Tiling (with extra condition)
- Each such tiling is realised by a covering



No perfect order is enforced.

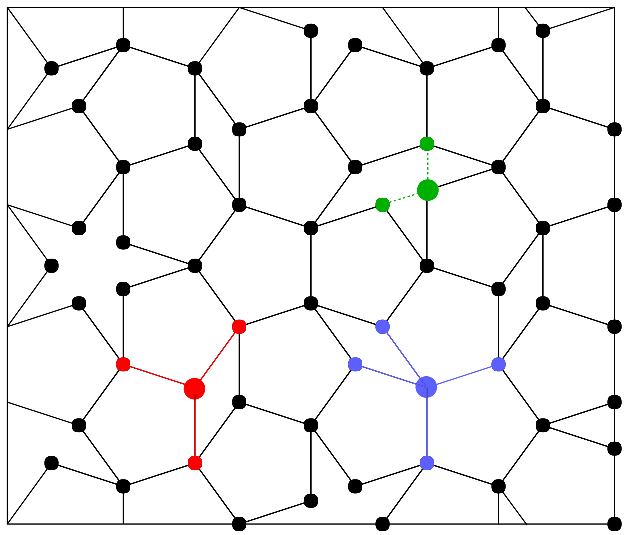
Highest cluster density realised in periodic approximant
$\rightarrow$ **crystalline ground state**.

Quasicrystal saved by entropic stabilisation.

How Many Coverings per Tiling

Four A-neighbors or two B-neighbors fix cluster orientation.

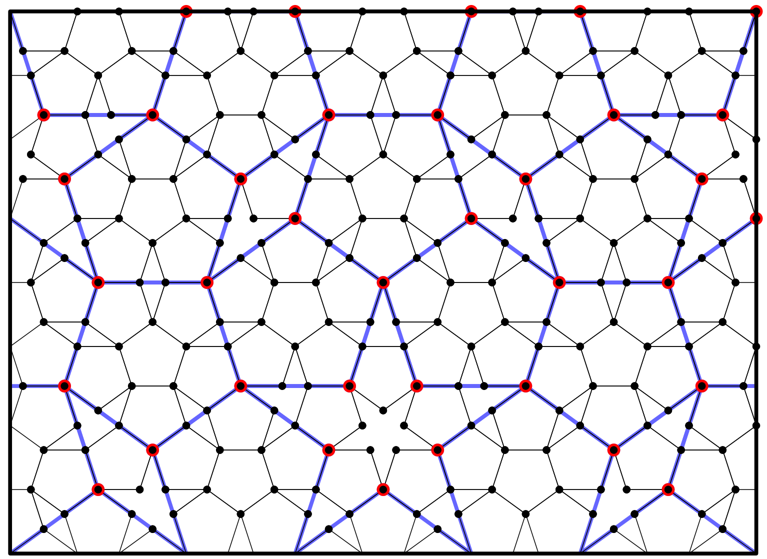
Only choice at obtuse corners of rhombi:



Two choices per rhombus.

Covering with Vertex Cluster

Vertex cluster covering is supertile random tiling:



Structure with maximal vertex cluster density is the same supertile random tiling.

Cluster density maximization orders the full random tiling to a supertile random tiling.

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Quasicrystals are often covered by a few characteristic motifs ("clusters").

Maximizing these leads to overlaps, correlations, and order.

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$\rightarrow$ ordering principle for quasicrystals.

More typical: no perfect order, but supertile random tiling ensemble.

Entropy contribution to free energy can then lead to quasicrystalline state (with disorder).