Energy-driven pattern formation: Optimal crystals

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It is amazing that even complex molecules like proteins crystallize without significant interference.

- The anti-AIDS drug ritonavir was discovered in 1992.
- From 1996 onwards the drug was sold in the form soft gelatin capsules.
- In 1998 the drug failed the dissolution test because a new crystal form of ritonavir precipitated.
- The observation triggered a complete withdrawal, redevelopment and reapproval of the drug.
Energy minimization

Standard modeling approach:

$$E_\Omega(u) \in \mathbb{R}$$

is the energy of a subsystem in a box $\Omega \subset \mathbb{R}^d$, $d \in \{2, 3\}$. Free energy:

$$f(\beta, \Omega) = - \log \left( \int_{\Omega^N} \exp(-\beta E_\Omega(u)) \, du \right)$$

The probability of a state $u$ at temperature $T$ is given by

$$P_{\Omega, T}(u) = \exp(-\beta E_\Omega(u) + f(\beta, \Omega)),$$

where $\beta = \frac{1}{k_B T}$ is the inverse temperature.

The study of the thermodynamic limit $N \to \infty$ with $|\Omega_N| = \rho N$ is a hard problem.

Easier: Exchange the limits $\beta \to \infty$, $N \to \infty$ and study the asymptotic behavior of the minimizers of $E_\Omega$ as $N \to \infty$. 
Assumption: $\rho = 1$, $N := \Omega \cap \mathcal{L}$, $\lim_{N \to \infty} \frac{1}{N}|\Omega_N| = 1$ and $E$ is permutation-invariant:

$$E(u_1, \ldots, u_N) = E(u_{\pi(1)}, \ldots, u_{\pi(N)})$$

for each permutation $\pi$.

A lattice $\mathcal{L} \subset \mathbb{R}^d$ is a crystalline ground state of $E$ if

$$e_0 := \lim_{N \to \infty} \frac{1}{N} \min_u E_{\Omega}(u) = \lim_{N \to \infty} \frac{1}{N} E_{\Omega}(\Omega \cap \mathcal{L}).$$
Models dominated by local interactions

**Strategy:** A groundstate is periodic if it is almost everywhere locally periodic.

Define the Cauchy-Born energy density function

\[
W^{CB}(F) = \lim_{N \to \infty} \frac{\det F}{N} E_{\Omega}(\Omega \cap F \mathcal{L})
\]

and the Cauchy-Born approximation

\[
E^{CB}_{\Omega} = \int_{\Omega} W(\nabla v(x)) \, dx,
\]

if \( v \) is piecewise affine and \( v(\mathcal{L}) = \{u_1, u_2, \ldots\} \).

\( E_{\Omega} \) is dominated by local interactions if

\[
E_{\Omega}(u) \geq \int_{\Omega} W(\nabla v) \, dx
\]

for suitable \( v \) (depends on triangulation).
Let $\Omega \subset \mathbb{R}^2$ bounded, $\mu, \nu \in \mathcal{P}(\Omega)$ probability measures. The associated Wasserstein-distance is defined as

$$\mathcal{W}^2(\nu, \mu) = \inf \left\{ \int_{\Omega} |x - y|^2 \, d\Psi(x, y) : \Psi \in \mathcal{P}(\Omega \times \Omega) \right\},$$

where

$$\int_{\Omega} \Psi(x, y) \, dx = \mu, \quad \int_{\Omega} \Psi(x, y) \, dy = \nu.$$ 

Energy (in 2 dim) if $|\Omega| = 1$:

$$F_\lambda(\mu) = \lambda \sum_{z \in \text{supp}(\mu)} \mu(\{z\})^{\frac{1}{2}} + \mathcal{W}^2(\text{Leb}_\Omega, \mu).$$

Key property: $\mathcal{W}^2$ is local.

$$\mathcal{W}^2(\text{Leb}_\Omega, \mu) = \int W(x, \nabla \nu)$$

if $\nu$ is induced by Voronoi tessellation.
Figure: An illustration of the appearance of a hexagonal pattern as $\lambda \to 0$. 
Diblock copolymer melts are well-known pattern formation systems.
Material parameters:
\( \chi \): Flory-Huggins interaction
\( N \): Index of polymerization
\( f \): Relative abundance
Theorem (Bourne/Peletier/T.’14)

A If $\Omega$ is a polygon with at most 6 sides, then

$$\lambda^{-\frac{4}{3}} F_\lambda \geq c_6,$$

where $c_6$ is the energy of a hexagon.

B If $\partial \Omega$ is Lipschitz, then

$$\lim_{\lambda \to 0} \inf \lambda^{-\frac{4}{3}} F_\lambda = c_6.$$

The limit is achieved by a scaled triangular lattice.
Configurational crystallization

Theorem

(a) If $F_{\lambda}(\mu) = \lambda^\frac{4}{3} c_6$, then $\mu$ is an atomic measure with all weights equal to 1, and $\text{supp}\mu$ a translated, rotated and dilated triangular lattice.

(b) Define the dimensionless defect of a measure $\mu$ on $\Omega$ as

$$d(\mu) := \lambda^{-\frac{4}{3}} F_{\lambda}(\mu) - c_6.$$ 

There exists $C > 0$ such that for $\lambda < C^{-1}$ and for all $\mu$ with $d := d(\mu) \leq C^{-1}$, $\text{supp}\mu$ is $O(d^{1/6})$ close to a triangular lattice.
Mathematical tools

Theorem (Kantorovich (1942), Optimal mass transportation)

If $\nu$ is absolutely continuous with respect to the Lebesgue measure, then for each $\mu$ there exists an optimal transport plan $T : \Omega \rightarrow \Omega$ such that $\mu$ is the push-forward of $\nu$ under $T$ and

$$\mathcal{W}^2(\nu, \mu) = \int_\Omega |x - T(x)|^2 \, d\nu(x).$$

Lemma (Fejes Tóth (1972))

If $\partial \chi$ is a polygon with $n$ sides, then

$$\inf_z \int_\chi |x - z|^2 \, dx \geq c_n |\chi|^\frac{1}{2},$$

where $c_n = \frac{1}{2n} \left( \frac{1}{3} \tan \frac{\pi}{n} + \cot \frac{\pi}{n} \right)$.

Equality is attained if and only if $\partial \chi$ is a regular $n$-gon.
Lemma

If $\mu$ is a minimizer of $E_\lambda$, then $\mu(\{z\}) > 0$ implies $\mu(\{z\}) > 2.4 \cdot 10^{-4}$.

The result is certainly not optimal and relies on the following upper bound bound on the size of holes:

$$\mu(B(z, R) \setminus \{z\}) > 0$$

if $\mu(z) > 0$ and $R > 3.3$. 

Most common crystalline lattices are fcc (face-centered cubic), hcp (hexagonally close packed) and bcc (body centered cubic).

Only fcc and hcp are close packings.
Many non-equivalent close packings can be constructed by stacking 2D triangular lattices.

An hcp-lattice is obtained if the particles in the third layer are on top of the particles in the first layer.

An fcc-lattice is obtained if the particles in the third layer are on top of the holes in the first and second layer. (ABABA... = hcp, ABCABC = fcc).

Third-nearest neighbors are closer in the hcp-lattice.
Two- and three-body energies

\[ E(Y) = \sum_{\{y, y'\} \subset Y} V_2(y, y') + \sum_{\{y, y', y''\} \subset Y} V_3(y, y', y''). \]

\( Y \subset \mathbb{R}^3 \) particle positions.

\( E \) invariant under rigid body motion:
\[ V_2(y, y') = V(|y - y'|), \]

The Lennard-Jones potential
\[ V_{LJ}(r) = r^{-12} - r^{-6} \]
accounts for van-der-Waals interactions at long distances.
**Theorem A.** (T. ’07)
Let $d = 2$, $\mathcal{L}$ be the triangular lattice and $\rho(r) = \min \{1, r^{-7}\}$. There exists an open set $\Omega \subset C^2_{\rho}([0, \infty))$ such that for all all $V_2 \in \Omega$ the identity

$$\lim_{n \to \infty} \min_{\#Y = n} \frac{1}{n} E(Y) = E_* = \min_{r} \frac{1}{2} \sum_{k \in \mathcal{L}\{0\}} V(r |k|)$$

holds.
Visualisation of $\Omega$

Example: Morse potential $V(r) = e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}$. 

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Theorem B. (Harris-T. ’14)
Let $d = 3$, $\mathcal{L}$ be the fcc lattice and $\rho(r) = \min \{1, r^{-10}\}$. There exists a set $\Omega \subset C^2_\rho([0, \infty)) \times C^2([0, \infty) \times [0, \infty))$ such that the projection of $\Omega$ to $C^2_\rho([0, \infty))$ is open and for all all $(V_2, V_3) \in \Omega$ the identity

$$\lim_{n \to \infty} \min_{\# Y = n} \frac{1}{n} E(Y) = E_*$$

$$= \min_r \left( \frac{1}{2} \sum_{k \in \mathcal{L} \setminus \{0\}} V(r \lvert k \rvert) + \frac{1}{6} \sum_{k, k' \in \mathcal{L} \setminus \{0\}} V_3(0, r k, r k') \right).$$

holds.
Theorem C. \( \mathcal{L} \) Bravais lattice, \( Y \subset \mathbb{R}^d \) countable and \( \mathcal{L} \)-periodic,

\[
\frac{1}{\# Y} E_{\text{per}}(Y) \leq E_*. 
\]

Then \( \frac{1}{\# Y} E_{\text{per}}(Y) = E_* \) and there exists dilation \( r > 0 \), translation \( t \in \mathbb{R}^3 \) and rotation \( R \in SO(d) \) such that

\[
R Y + t = r \mathcal{L}_{\text{fcc}} \text{ or } r \mathcal{L}_{\text{tri}}.
\]
Dislocations in the case of pair interaction potentials

Equilibria can have many defects.

Recent results: Alicandro-De Luca-Garroni-Ponsiglione, Ortner-Hudson
Dislocations in the case of pair interaction potentials

Equilibria can have many defects.

Ground state energy $E_{\text{min}} = -8.642719 \times 10^1$ for $N = 121$.

Recent results: Alicandro-De Luca-Garroni-Ponsiligone, Ortner-Hudson
Previous results

- Radin ’79 Periodicity of groundstates for Lennard-Jones type potentials (1d)
- Radin ’81 Periodicity of triangular lattice for compactly supported potentials (2d)
- Friesecke-T’02 Periodicity of ground states for mass-spring models (2d)
- Suto ’05 Stealthy potentials (3d)
- T’06 Proof of minimality of the triangular lattice for Lennard-Jones type models (2d)
- E-Li ’08 Minimality of hexagonal lattice for three-body interactions (2d)
Strategy: A groundstate is periodic if it is almost everywhere \textbf{locally} periodic. \rightarrow Local problems

\textbf{Step 1:} Local analysis: Neighborhood graph, defects.

\textbf{Step 2:} Treat non-local terms using cancelations and rigidity estimates
Step 1: Local analysis

• Minimum particle spacing:
  \[|y_i - y_{i'}| > 1 - \alpha \text{ for all } i \neq i'\]
  since particles can be moved to infinity.

• Construction of a graph:
  \[
  \{i, i'\} \in \mathcal{B} \iff |y_i - y_{i'}| \in (1 - \alpha, 1 + \alpha)
  \]

• Musin’s (2005) proof of the 3d-kissing problem:
  \[
  \#\{b \in \mathcal{B} \mid i \in b\} \leq 12
  \]
**Theorem.** (Harris/Tarasov/Taylor/T.'13)
If $S$ is a unit sphere in $\mathbb{R}^3$ and $S_1 \ldots S_n$ pairwise exclusive unit spheres touching $S$. Then the number of tangency points is smaller or equal 36.
Equality is obtained if and only if $n = 12$ and $S_1 \ldots S_n$ form the corners of a either a cuboctahedron or a twisted cuboctahedron.

**Conjecture:** Let $S_1, S_2$ be two touching unit spheres in $\mathbb{R}^3$. Then there can be at most 18 pairwise exclusive unit spheres touching $S_1$ or $S_2$. 
Figure: Contact graphs of $Q_{co}$ and $Q_{tco}$ respectively.
Sketch of the proof

There are 1,430,651 2-connected graphs with 12 vertices, at least 24 edges, at most 5 edges adjacent to any given vertex. Contact graphs are those graphs where edges are induces by vertex positions. For each contact graph we define angles $u_j \in [0, 2\pi]$ subtended by edges. The angles satisfy linear inequalities such as

$$\min_j u_j \geq \arccos\left(\frac{1}{3}\right),$$

$$\sum_{j \text{ adjacent to vertex } i} u_j = 2\pi,$$

...:

Only for two graphs the corresponding linear programming problems admit a solution.
Step 2: Nonlocal terms

Two different ideas are needed.

A) Discrete rigidity estimates

B) Cancelation of the ghost forces

Use geometric rigidity of the system in order to control errors:

If the small triangles are undistorted, then the big triangle is undistorted.
Continuum rigidity results

\[
\min_{R \in S(d)} \int_{\Omega} |\nabla u - R|^2 \, dx \leq C(\Omega) \int_{\Omega} |\nabla u - SO(d)|^2 \, dx.
\]

(Friesecke, James & Müller, CPAM 2002). The rigidity constant \(C(\Omega)\) is invariant under rotations, dilations and translations:

\[
C(R\Omega + t) = C(\Omega) \text{ for all } R = \lambda Q, \lambda \in \mathbb{R}, Q \in O(d), t \in \mathbb{R}^d
\]
Summary

- Convergence of the minimum energy for block co-polymer model
- Methods from optimal transportation theory
- Open set of interaction potentials which admits periodic (fcc) minimizers in $\mathbb{R}^3$
- Result based on mixture of results from Geometry and PDE theory.
- Open problem: Finite temperature.

$$\lim_{|\Omega| \to \infty} p_{\beta, \Lambda}(Y) = \lim_{|\Lambda| \to \infty} \exp(-\beta E(Y) + f(\beta, \Omega)) = ?$$
Finite temperature: $\beta \ll 1$

Gas phase, dimension irrelevant

Expected: The dimension $d$ matters if $\beta \gg 1$. 
Finite temperature: $\beta \gg 1$

$d = 3$: Long-range order, one large cluster iff $\beta > \beta_{\text{crit}}(\rho)$  
$d = 2$: Local order, one large cluster iff $\beta > \beta_{\text{crit}}(\rho)$. No long-range order due to the Mermin-Wagner Theorem  
$d = 1$: Several finite clusters, no phase transition. Cluster sizes are bounded.
Local (orientational) order
Let \( \varphi \) be testfunction with compact support such that
\[
\int_{SO(d)} \varphi(R x) = 0
\]
and define for \( R \in SO(d) \)
\[
f(R) = \frac{1}{|Y|} \sum_{y \neq y' \in Y} \varphi(R(y' - y)).
\]

\( Y \) exhibits local order if \( f(R) = O(1), \, |Y| \gg 1 \).

Long range order
Let \( \varphi \) be a \( \mathcal{L} \)-periodic testfunction such that
\[
\int_{\mathbb{R}^d/\mathcal{L}} \varphi = 0
\]
and define for \( R \in SO(d) \)
\[
g(R) = \frac{1}{|Y|^2} \sum_{y \neq y' \in Y} \varphi(R(y' - y)).
\]

\( Y \) exhibits long-range order if \( g(R) = O(1), \, |Y| \gg 1 \).
Local and long-range order (ctd)

Expected:

If $\beta \ll 1$ there is neither local, nor long range order for all $d > 1$.

If $\beta \gg 1$ there exists local order, but not global order for $d = 2$ and global order for $d = 3$. 
Surface energy for $d = 1$

Binding energy per particle:

$$e_0 = \lim_{N \to \infty} \frac{1}{N} \min_{\#Y=N} E(Y) < 0.$$  

Surface energy:

$$e_{\text{surf}} = \lim_{N \to \infty} \left( \min_{\#Y=N} E(Y) - N e_0 \right) > 0.$$  

The surface energy accounts for missing bonds and surface relaxation **and is different from** $-e_0$.  

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Cluster size distribution

A configuration $Y = \{y_1 < y_2 < \ldots < y_N\} \subset \Lambda$ is decomposed into clusters $C_i$ which have the properties

- $y_j, y_{j+1} \in C_i$ then $y_{j+1} - y_j < R$
- $Y = \bigcup_i C_i$
- $\text{dist}(C_{i_1}, C_{i_2}) \geq R$ if $i_1 \neq i_2$.

$$\nu_\beta(k) = \lim_{N \to \infty} \frac{\#\{\text{clusters } C : \#C = k\}}{\#\{\text{clusters}\}} \quad \text{(cluster length histogram)}$$
Work in progress. (Jansen-König-Schmidt-T’14)
Assume $v(r) = r^{-2} p - r^{-p}$ (Lennard-Jones potential),

- $\rho < \frac{1}{a}$
- $p(\beta, \rho)$ chosen so that $p^{-1} \nu_{\beta}(\cdot / p)$ is tight and non-singular as $\beta \to \infty$.

Then

- $\lim_{\beta \to \infty} \frac{1}{\beta} \log(p(\beta, \rho)) = -\frac{1}{2} \text{e}_{\text{surf}}$,
- $\lim_{\beta \to \infty} p^{-1} \nu_{\beta}(\cdot / p) = \exp_1$. 
L. Harris & F. T.  
*3d Crystallization: The FCC case.*  
Submitted for publication.

D. Bourne, M. Peletier & F. T.  
Optimality of the Triangular Lattice for a Particle System with Wasserstein Interaction.  

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In preparation.