Isoperimetric problems on periodic lattices

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Isoperimetric Problems @Pisa

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The Isoperimetric Problem

"Determine, among all sets $E \subset \mathbb{R}^d$ of given d-volume $|E|$, the ones that minimize the $(d-1)$-measure of the boundary (aka, the *perimeter*)"

Isoperimetric inequality in $\mathbb{R}^d$

$E \subset \mathbb{R}^d$ measurable with $|E| < +\infty$, then

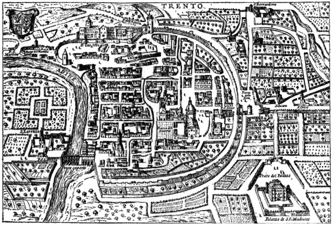
$$d\,\omega_d^{\frac{1}{d}}\,|E|^{\frac{d-1}{d}} \leq P(E)$$

with equality if and only if E is a ball, up to negligible sets.

Note that the left-hand side of the inequality is the perimeter of a Euclidean ball with volume $|E|$.

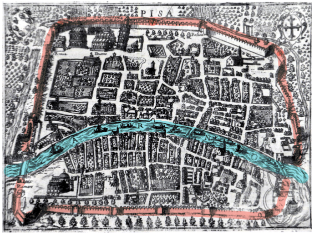
Isoperimetry and...the shape of cities

Pisa (1616)



Trento (1761)

Isoperimetry and...the shape of cities



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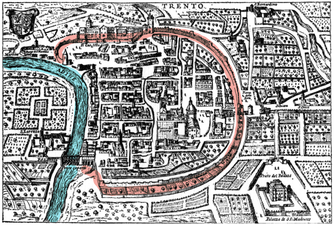
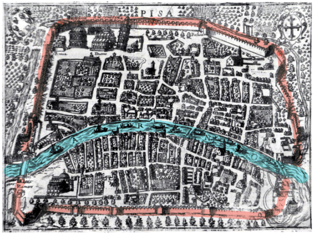
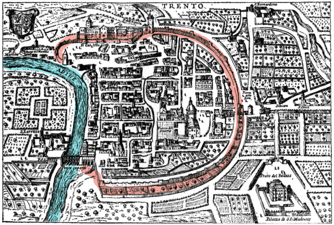


Trento (1761)

Isoperimetry and...the shape of cities



Pisa (1616)



Trento (1761)

Queen Dido clearly has a preference...

At smaller scales...crystallization!

i.e., the formation of crystals, nanoparticles, etc.

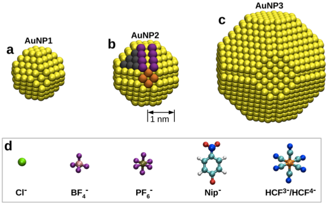


Figure 1: a)-c) Snapshots of gold nanoparticles, AuNP1, AuNP2, AuNP3, respectively. The NP bare radii from left to right are $R_{\mathrm{NP}} = 0.82, 1.02, 1.84$ nm, respectively, which are defined as the shortest distance between the center of AuNP and the (100) facets. The color code in b) stands for the representative (100) facet (orange), (111) facet (gray), and (110) facet (purple). d) Anions studied in our simulations: Cl^-, $BF_4{}^-$, $PF_6{}^-$, Nip^-, HCF^{3-}/HCF^{4-} (from left to right). Na^+ ions were used as the cations (counterions) for all the simulations.

(the second picture is taken from [Li-Ruiz-Kanduc-Dzubiella, 2020])

Outline of the talk

1. Wulff problem and crystallization in 2D

2. The quantitative isoperimetric inequality

3. Wulff crystals and maximal fluctuations on 2D lattices

4. Crystallization in 3D lattices

Wulff problem and crystallization in 2D

The Wulff problem - continuum setting

"The Crystal tends to assume a form which corresponds to the minimum of the energy and will try to take advantage of any possibility to do so" [G. Wulff (1901)]

"For materials with small grains the bulk energy is negligible with respect to the contribution of the surface tension" [C. Herring (1951)]

The **Wulff problem**:

$$\min\left\{\int_{x\in\partial^* E}\varphi(\nu_E(x))\,d\,\mathcal{H}^{d-1}(x) :\, |E| = const.\right\}$$

$\varphi : \mathbb{R}^d \to [0, +\infty)$, convex, 1-hom and $0 < c \leq \varphi(\nu) \leq C$, for $\nu \in S^{d-1}$.

If $\varphi \equiv 1$ then the Wulff problem reduces to the Isoperimetric problem.

The Wulff problem - microscopic origin and crystallization - I

Is there a microscopic justification for the anisotropy of the surface tension?

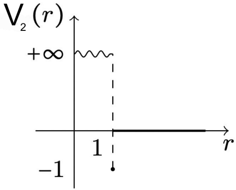
The arrangement of atoms results from a geometric optimization process:

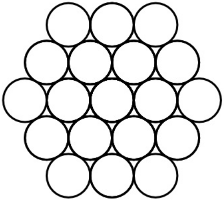
1. Identify a configuration X of N atoms by their positions $X = \{x_1, x_2, \ldots, x_N\}$
2. Consider a suitable configurational energy H_N
3. Prove that the minimizers of H_N are subsets of a periodic lattice

Such a process (problem) is also known as Crystallization

The Wulff problem - microscopic origin and crystallization - II

$d = 2, \quad X = \{x_1, x_2, \ldots, x_N\}, \quad H_N(X) = \sum_{i \neq j} V_2(|x_i - x_j|)$





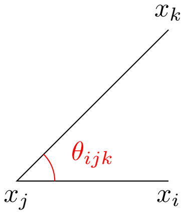
Radius $r = \frac{1}{2}$ and centres at X

Theorem (Harborth '74, Heitmann-Radin '80, De Luca-Friesecke '17)

Minimizers of H_N are subsets of the triangular lattice

The Wulff problem - microscopic origin and crystallization - III

$$d = 2, \quad H_N(X) = \sum_{i \neq j} V_2(|x_i - x_j|) + \sum_{i \neq j \neq k} V_3(\theta_{ijk}), \qquad V_3(\theta) \geq 0$$



θ_{ijk} angle between $x_i - x_j$ and $x_k - x_j$

Theorem (Mainini-Stefanelli '14, Mainini-Piovano-Stefanelli '14)

Minimizers of H_N are subsets of a lattice:

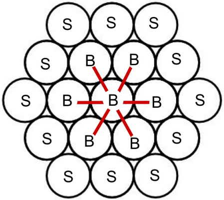
$$V_3^{-1}(0) = \begin{cases} \{2\pi/3, 4\pi/3\} & \Longrightarrow \text{ honeycomb} \\ \{\pi/2, \pi, 3\pi/2\} & \Longrightarrow \text{ square} \end{cases}$$

The Wulff problem - microscopic origin and crystallization: $N \to \infty$

Focus on the case $d = 2$ and $V_3 = 0$

The minimal energy developes as

$$H_N(X) \simeq \underbrace{-6N}_{\textbf{B}\text{ulk}} + C \underbrace{\sqrt{N}}_{\textbf{S}\text{urface}}$$



What happens to $\dfrac{H_N(X) + 6N}{\sqrt{N}}$ as $N \to \infty$?

First results **assume crystallization**
More recent results **DO NOT assume crystallization**

The Wulff problem - microscopic origin and crystallization: $N \to \infty$

$X = \{x_1, x_2, \ldots, x_N\}, \quad H_N(X) = \sum_{i \neq j} V_2(|x_i - x_j|)$

Scaled empirical measures: $\mu_N = \frac{1}{N} \sum_{i=1}^{N} \delta(N^{-1/2} x_i)$

Theorem (Yeung-Friesecke-Schmidt (CVPDE 2012))

$\frac{H_N(X)+6N}{\sqrt{N}} \leq C \Longrightarrow \exists\, \tau_N \in \mathbb{R}^2 :$ u.t.s. $\mu_N(\cdot + \tau_N) \overset{*}{\rightharpoonup} \frac{2}{\sqrt{3}} \mathcal{L}^2 \llcorner E,\ \mathcal{L}^2(E) = \frac{\sqrt{3}}{2}$

Assuming crystallization on the triangular lattice

$\Downarrow$

Theorem (Yeung-Friesecke-Schmidt (CVPDE 2012))

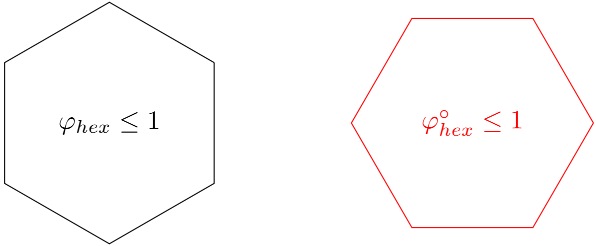
$$\Gamma\text{-}\lim_N \frac{H_N(X) + 6N}{\sqrt{N}} = \int_{\partial^* E} \varphi_{hex}(\nu_E)\, d\mathcal{H}^1 =: \mathcal{F}(E)$$

As a consequence: if X minimizes H_N, then $\mu_N(\cdot + \tau_N) \overset{*}{\rightharpoonup} \frac{2}{\sqrt{3}} \mathcal{L}^2 \llcorner W$ where W is the Wulff crystal of $\mathcal{F}$ with $\mathcal{L}^2(W) = \sqrt{3}/2$.

The Wulff problem - microscopic origin and crystallization: $N \to \infty$

The Wulff crystal W is homothetic to

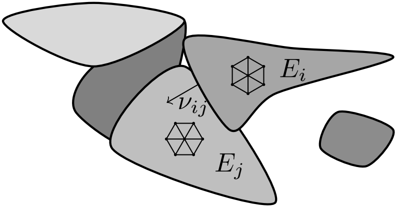
$$\{x \in \mathbb{R}^2 : \; x \cdot \nu \le \varphi_{hex}(\nu), \; \forall \nu \in S^1\} \; = \; \{x \in \mathbb{R}^2 : \; \varphi^\circ_{hex}(x) \le 1\}$$



The Wulff problem - microscopic origin and crystallization: $N \to \infty$

NOT assuming crystallization

Configurations with bounded energy may form **polycrystals**



Theorem (Friedrich-Kreutz-Schmidt (ARMA 2020))

$$\Gamma\text{-}\lim_{N} \frac{H_N(X) + 6N}{\sqrt{N}} = \sum_{i,j=1}^{M} \int_{\partial^* E_i \cap \partial^* E_j} \varphi_{ij}(\nu_{ij})\, d\,\mathcal{H}^1$$

Single crystal: De Luca - Novaga - Ponsiglione JNLS (2019)
With elasticity: Lauteri - Luckhaus (2016) - Read-Shockley formula

The Quantitative Isoperimetric Inequality

The Quantitative Isoperimetric Inequality

$E \subset \mathbb{R}^d$ with $0 < |E| < \infty$, B ball centered at 0, such that $|B| = |E|$.

Isoperimetric deficit:

$$\delta(E) = \frac{P(E) - P(B)}{P(B)}$$

Isoperimetric Inequality rephrased

For all $E \subset \mathbb{R}^d$ with $0 < |E| < \infty$ it holds

$$\delta(E) \geq 0$$

Moreover $\delta(E) = 0$ if and only if $E = B$ up to translations and null sets.

The Quantitative Isoperimetric Inequality

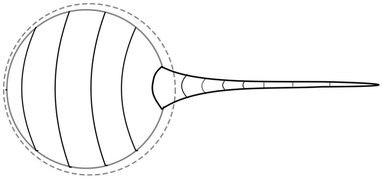
$\delta(E) = \frac{P(E)-P(B)}{P(B)}$

$$\text{if} \quad \delta(E) \to 0 \quad \text{then} \quad E \to B \ \text{(up to translations)}$$

Question: is there a quantitative relation between the isoperimetric deficit and some distance from spherical shapes?

Fraenkel's asymmetry index:

$$\alpha(E) = \inf \left\{ \frac{|E \,\Delta\, (x+B)|}{|B|} \, : \, x \in \mathbb{R}^d \right\} \in [0,2)$$



The Quantitative Isoperimetric Inequality

Sharp Quantitative Isoperimetric Inequality

There exists $C = C(d) > 0$ such that for all $E \subset \mathbb{R}^d$ with $0 < |E| < \infty$ it holds

$$\delta(E) \geq C \cdot \alpha^2(E)$$

A super-short bibliography on QII

- Fuglede (1989): nearly-spherical sets in $\mathbb{R}^d$
- Hall, Hayman, Weitsmann (1991): general case in $\mathbb{R}^2$
- Hall (1992): sets with axial symmetry in $\mathbb{R}^d$, then subopt. exp. 4
- Fusco, Maggi, Pratelli (2008): general case in $\mathbb{R}^d$ (via symmetrization)
- Figalli, Maggi, Pratelli (2010): general case in $\mathbb{R}^d$ (also for Wulff ineq.) (via optimal transportation)
- Cicalese, L. (2012): general case in $\mathbb{R}^d$ (via regularity theory for minimal surfaces)
- Acerbi-Fusco-Morini, Fusco-Julin, Cabre'-Ros-Oton-Serra, Chodosh-Engelstein-Spolaor,...: generalisations, pde methods

Wulff crystals and maximal fluctuations in 2D lattices

The Wulff problem on a lattice

Assume the crystallization on a lattice $\mathcal{L} \subset \mathbb{R}^2$ of ligancy l
(e.g., $l = 6$ for the triangular lattice)

Gibbs picture: the shape of a crystal made of N atoms in the lattice $\mathcal{L}$ is obtained minimising the excess energy

$$\mathcal{E}_N(X) = H_N(X) + l \cdot N$$

Denoting by $b(x) = l - \#\{y \in X : \mathrm{d}(x, y) = 1\}$ the number of loose bonds of $x \in X$

$$\mathcal{E}_N(X) = \sum_{i=1}^{N} b(x_i)$$

$\mathcal{E}_N$ is a discrete perimeter. Its minimisation is a discrete Wulff problem.

This problem is known as the edge isoperimetric problem

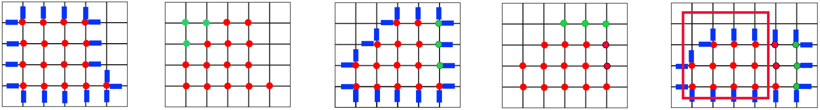
The Wulff problem on a **2D** lattice and the $N^{3/4}$ law

Theorem (Yeung-Friesecke-Schmidt, Schmidt, Mainini-Stefanelli, Mainini-Piovano-Stefanelli, Davoli-Piovano-Stefanelli,...)

Maximal fluctuation: The minimisers of $\mathcal{E}_N$ differ from the continuum Wulff crystal by at most $O(N^{3/4})$ atoms

The proof goes via delicate ad hoc estimates, or as a corollary of a discrete isoperimetric inequality

Fluctuation



Maximal fluctuations and asymmetry estimates

Can we relate fluctuations of discrete Wulff crystals to the sharp quantitative Wulff inequality in the continuum?

Observe that:

1. The discrete Wulff crystals minimize the discrete energy $\mathcal{E}_N$
2. The discrete Wulff crystals converge to the continuum Wulff crystal W
3. The continuum Wulff crystal minimizes a continuum energy $\mathcal{F}$ (anisotropic perimeter)
4. The Sharp Quantitative Wulff Inequality:

$$\alpha^2(E) \lesssim \delta(E) := \frac{\mathcal{F}(E) - \mathcal{F}(W)}{\mathcal{F}(W)}$$

that is

$$\inf_{x \in \mathbb{R}^d} |E \, \Delta(x + W)| \lesssim |W| \sqrt{\frac{\mathcal{F}(E) - \mathcal{F}(W)}{\mathcal{F}(W)}}$$

Quantitative closeness

For $x \in \mathcal{L}$, $V(x)$ is the Voronoi cell centered at x

For $X \in \mathcal{X}(\mathcal{L}) = \{\text{subsets of } \mathcal{L}\}$, $V(X) = \bigcup_{x \in X} V(x)$ is the Voronoi set associated to X

Set $\mathcal{M}(\mathbb{R}^d)$ measurable sets in $\mathbb{R}^d$, define $\zeta : \mathcal{X}(\mathcal{L}) \to \mathcal{M}(\mathbb{R}^d)$ and call $\zeta(X)$ representative of X in the continuum.

Definition (Quantitative Closeness)

We say that $\mathcal{E}_N$ is quantitatively close to $\mathcal{F}$ with parameters $\alpha_N, \beta_N, \gamma_N, \delta_N$ if there exists $\zeta : \mathcal{X}(\mathcal{L}) \to \mathcal{M}(\mathbb{R}^d)$ such that, given $X \in \mathcal{X}(\mathcal{L})$ satisfying $\mathcal{E}_N(X) - \min \mathcal{E}_N(X) \leq \alpha_N$,

1. $\mathcal{F}(\zeta(X)) - \mathcal{E}_N(X) \leq \beta_N$ u. b. (disc to cont energy error)
2. $\min \mathcal{E}_N - \min \mathcal{F} \leq \gamma_N$ l. b. on infima (rate of convergence)
3. $|\zeta(X) \, \Delta \, V(X)| \leq \delta_N$ fidelity error of the disc to cont representation

Quantitative closeness

Proposition (Cicalese - L., CMP 2019)

Assume that $\mathcal{F}$ satisfies a quantitative inequality in the form

$$\inf_{x\in\mathbb{R}^d} |E \,\Delta\, (x + W_v)| \le v\,\varphi\left(\frac{\mathcal{F}(E) - \mathcal{F}(W_v)}{\mathcal{F}(W_v)}\right)$$

with φ an increasing modulus of continuity and $\mathcal{F}(W_v) = \min_{|E|=v} \mathcal{F}(E)$. If $\mathcal{E}_N$ is quantitatively close to $\mathcal{F}$ with parameters $\alpha_N, \beta_N, \gamma_N, \delta_N$, then, setting $|\zeta(X)| = v$, it holds

$$\min_{x\in\mathbb{R}^d} |V(X) \,\Delta\, (x + W_v)| \le \delta_N + v\,\varphi\left(\frac{\alpha_N + \beta_N + \gamma_N}{\mathcal{F}(W_v)}\right)$$

Quantitative closeness and maximal fluctuation of the Wulff crystal

Proposition (Cicalese - L., CMP 2019)

Let $\mathcal{L}$ be the triangular, square, or honeycomb lattice. Let $X \in \mathcal{X}(\mathcal{L})$ be such that $\mathcal{E}_N(X) - \min \mathcal{E}_N(X) \leq \alpha_N$. Then there exists $C > 0$ such that

$$\min_{x \in \mathbb{R}^d} |V(X) \, \Delta \, (x + W_N)| \leq C \, N^{3/4} \sqrt{1 + \alpha_N}$$

In particular this gives the $N^{3/4}$-law in the case of minimisers ($\alpha_N = 0$)

The proof for $\mathcal{L} = \mathbb{Z}^2$

$\mathbb{Z}^2$ has ligancy $l = 4$.

For $x \in X = \{x_1, x_2, \ldots, x_N\}$ the number of loose bonds is $b(x) = 4 - \#\{y \in X : \mathrm{d}(x, y) = 1\}$ and the energy

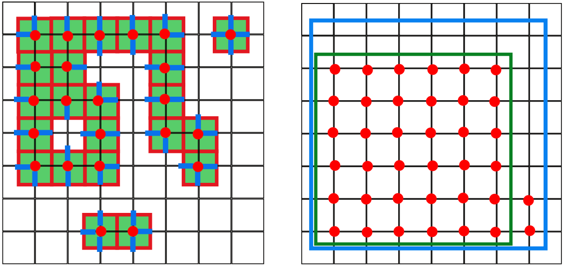
$$\mathcal{E}_N(X) = H_N(X) + 4N = \sum_{i=1}^{N} b(x_i)$$

For $\mathcal{F}(E) = \mathcal{P}_1(E) = \int_{\partial^* E} \|\nu\|_1 \, d\,\mathcal{H}^1$ it holds (Figalli-Maggi-Pratelli 2010)

$$\inf_{x \in \mathbb{R}^d} |E \, \Delta \, (x + W_v)| \leq v \, \varphi \left(\frac{\mathcal{P}_1(E) - \mathcal{P}_1(W_v)}{\mathcal{P}_1(W_v)} \right)$$

with $\varphi(x) = c_1 \sqrt{x}$ and $W_v = v^{1/2} \left[-\frac{1}{2}, \frac{1}{2}\right]^2$

The proof for $\mathcal{L} = \mathbb{Z}^2$



$V(x) = x + \left[-\frac{1}{2}, \frac{1}{2}\right]^2$ and $\zeta(X) = V(X)$, hence $\mathcal{E}_N(X) = \mathcal{P}_1(\zeta(X))$

For $k : k^2 \leq N < (k+1)^2$ it holds
$\min_{Y \in \mathcal{X}} \mathcal{E}_N(Y) - \min_{|F|=N} \mathcal{P}_1(F) \leq 4(k+1) - 4\sqrt{N} \leq 4$

$\mathcal{E}_N$ is quantitatively close to $\mathcal{P}_1$ with parameters $\alpha_N, \beta_N = 0, \gamma_N = 4, \delta_N = 0$.

The case $\mathcal{L} = \mathbb{Z}^d$

Proposition (Cicalese - L., CMP 2019)

Let $\mathcal{L} = \mathbb{Z}^d$ and let $X \in \mathcal{X}(\mathcal{L})$ be such that $\mathcal{E}_N(X) - \min \mathcal{E}_N(X) \leq \alpha_N$. Then there exists $C > 0$ such that

$$\min_{x \in \mathbb{R}^d} |V(X)\, \Delta (x + W_N)| \leq C\, N^{1-\frac{1}{2d}} \sqrt{1 + \alpha_N}$$

This result is **not optimal** for minimizers in $\mathbb{Z}^d$

Using discrete rearrangements for minimizers it can be proven that

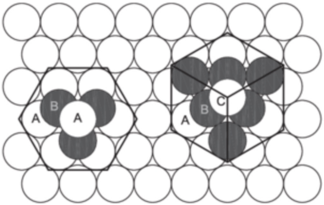
- the $N^{3/4}$ estimate is optimal on $\mathbb{Z}^3$
  E. Mainini, P. Piovano, B.Schmidt, and U. Stefanelli (JSP 2019)
- the sharp scaling law in $\mathbb{Z}^d$ is $N^{\zeta(d)}$ with $\zeta(d) = \frac{d-1+2^{1-d}}{d}$
  E.Mainini and B. Schmidt (CMP 2020)

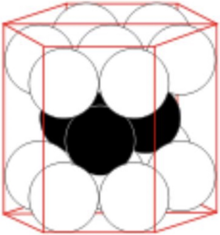
Crystallization in 3D lattices

The 3D case - Optimal packing

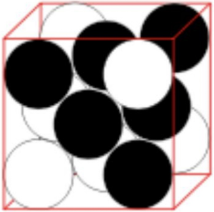
Theorem (Kepler's conjecture - Hales, 1998-2017)

No packing of congruent balls in $\mathbb{R}^3$ has density greater than that of the *Face-Centered Cubic* (FCC) packing.





HCP



FCC

the *Hexagonal Closed Packing* (HCP) lattice and any regular stacking of triangular lattices have the same density of the FCC lattice

The 3D case - FCC and HCP as $N \to \infty$

The FCC and HCP lattices have ligancy $l = 12$.

The loose bonds at x are $b(x) = 12 - \#\{y \in X : \mathrm{d}(x, y) = 1\}$ and the excess energy

$$\mathcal{E}_N(X) = H_N(X) + 12 \cdot N = \sum_{i=1}^{N} b(x_i)$$

On minimizers $\mathcal{E}_N$ scales as

$$\mathcal{E}_N(X) \simeq C \cdot N^{2/3}$$

We are interested in

$$\Gamma\text{-}\lim_{N \to \infty} N^{-2/3} \cdot \mathcal{E}_N(X)$$

The 3D case - from edge–isoperimetric to Wulff pbs

Let $\mathcal{L}$ be either FCC or HCP.

Take $X \subset N^{-1/3}\mathcal{L}$.

$V(X)$ = union of Voronoi cells centered at each $x \in X$.

Note that $|V(X)| = c(\mathcal{L})$ for some explicit constant $c(\mathcal{L})$.

Consider the scaled energy

$$E_{\mathcal{L},N}(V) := \begin{cases} N^{-2/3}\,\mathcal{E}_N(X) & \text{if } V = V(X) \\ +\infty & \text{otherwise} \end{cases}$$

The 3D case - from edge–isoperimetric to Wulff pbs

$$E_{\mathcal{L},N}(V) := \begin{cases} N^{-2/3}\,\mathcal{E}_N(X) & \text{if } V = V(X) \\ +\infty & \text{otherwise} \end{cases}$$

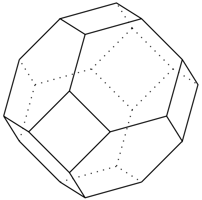
Theorem (Cicalese-Kreutz-L.)

There exists a convex, 1-homogeneous, non-negative, and explicitly computable function $\varphi_{\mathcal{L}}$ such that w.r.t. the strong L^1_{loc}-topology

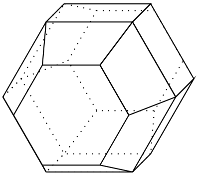
$$\Gamma\text{-}\lim_{N\to\infty} E_{\mathcal{L},N}(V) = \begin{cases} \int_{\partial^* V} \varphi_{\mathcal{L}}(\nu)\, d\mathcal{H}^2 & \textit{if } \chi_V \in BV_{loc}(\mathbb{R}^3) \\ +\infty & \textit{otherwise.} \end{cases}$$

Moreover, if $\{V_N = V(X_N)\}_N$ is such that $\sup_N E_{\mathcal{L},N}(V_N) < +\infty$, then it is relatively compact in $BV_{loc}(\mathbb{R}^3)$. Finally, if X_N minimizes E_N, then up to translations V_N converges to $W_{\mathcal{L}}$, the Wulff crystal associated to $\varphi_{\mathcal{L}}$ with $|W_{\mathcal{L}}| = c(\mathcal{L})$.

The 3D case - Wulff crystals for FCC and HCP



W_{FCC} - (trunc. octahedron)



W_{HCP} - (trunc. hex. bi-pyramid)

Observation: the isoperimetric ratios $m_{\mathcal{L}} = \frac{\mathcal{F}(W_{\mathcal{L}})}{|W_{\mathcal{L}}|^{2/3}}$ of the Wulff crystals are not equal:

$$m_{FCC} \simeq 99.5\% \, m_{HCP}$$

This gives theoretical support to the experimental evidence of crystallization occurring more often on FCC than on HCP!

The 3D case - Strategy of the proof

- Compactness more delicate than in 2D because of lack of uniform bounds on the diameter of V_N.
  Adapt to the discrete setting a well-known concentration-compactness argument leading to strong L^1 convergence up to translations.
- Γ-convergence adapting Alicandro-Cicalese-Ruf (ARMA, 2015) to obtain an asymptotic homogenization formula for $\varphi_{\mathcal{L}}$
- Via Chambolle & Kreutz (2021) $\varphi_{\mathcal{L}}$ can be computed via a cell formula.
- Solve a finite–dimensional convex optimization problem to get $\varphi_{\mathcal{L}}$.

Thanks for your attention