Crystallization and coarse graining for particles governed by pairwise interactions

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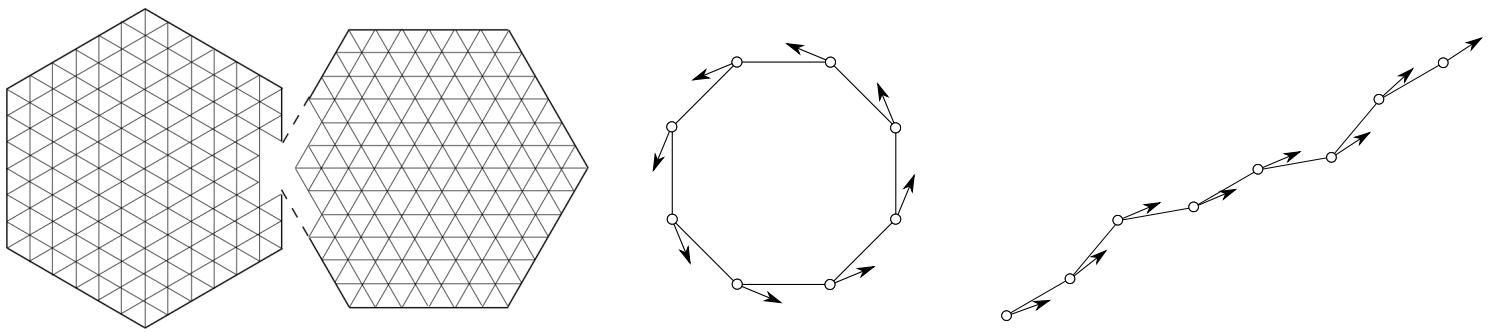
(joint works with with V. Crismale, L. De Luca, A. Kubin, A.Ninno, M. Novaga)



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The crystallization problem

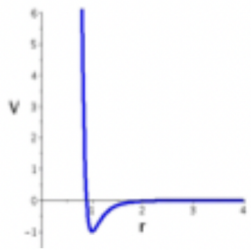
Q: Why atoms at very low temperature arrange into periodic lattices (microscopically) with specific shape (macroscopically)?

Simple variational models: 1D or 2D, zero temperature, pairwise interactions.

Given $X \subset \mathbb{R}^n$ finite, $E_V(X) := \frac{1}{2} \sum_{\substack{x,y \in X \\ x \neq y}} V(|x-y|)$.

Goal: Find the minimizers (or the limit behaviour for large number of particles).

Usually, V is the Lennard-Jones potential $V(r) = r^{-12} - 2r^{-6}$.



Gardner-Radin, 1979: In 1D, as $N \to +\infty$, X_N converges to a chain of equi-spaced particles.

Theil, 2006: In 2D, under some growth and convexity/concavity assumptions on V, the regular triangular lattice provides the best asymptotic energy density.

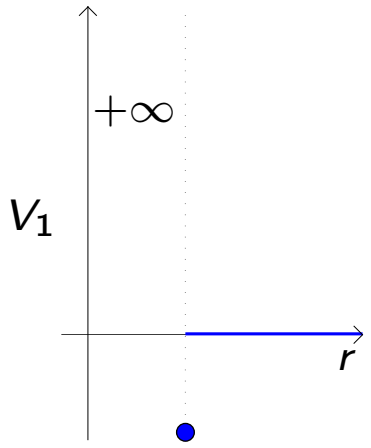
The Heitmann-Radin model: Sticky disc energy

For $N \in \mathbb{N}$, the energy of a configuration $X_N := \{x_1, \dots, x_N\} \subset \mathbb{R}^2$ is defined by

$$E^{\mathrm{HR}}(X_N) := \frac{1}{2} \sum_{i \neq j} V_1(|x_j - x_i|)\,.$$

where V_1 is the Heitmann-Radin sticky disc potential

$$V_1(r) := \begin{cases} +\infty & \text{if } r < 1\,, \\ -1 & \text{if } r = 1\,, \\ 0 & \text{if } r > 1\,. \end{cases}$$



Finite crystallization: For every $N \in \mathbb{N}$, the minimizers of E^{HR} among the configurations X with $\sharp X = N$ lie on the $\triangle$ lattice (Heitmann-Radin, 1980);

Macroscopic shape of the minimizers and $N^{\frac{3}{4}}$ law: Minimizers converge to the regular hexagon and deviate from it by at most $CN^{\frac{3}{4}} + o(N^{\frac{3}{4}})$ (Au Yeung-Friesecke-Schmidt, 2012, Schmidt, 2013, Davoli-Piovano-Stefanelli, 2017, Cicalese-Leonardi, 2019).

Quasi minimizers for E^{HR}

Energy per particle in the infinite regular triangular lattice: kissing number $= 6$; energy per particle $= -3$.

Total Energy of a finite crystal $= -3N +$ Surface Energy $\sim -3N + \sqrt{N}$.

Pb: What happens to configurations having a perimeter scaling energy?

Scaling: Set $V_\varepsilon(r) := V_1(\frac{r}{\varepsilon})$, i.e., $V_\varepsilon(r) := \begin{cases} +\infty & \text{if } r < \varepsilon\,, \\ -1 & \text{if } r = \varepsilon\,, \\ 0 & \text{if } r > \varepsilon \end{cases}$ and

$E_\varepsilon^{\mathrm{HR}}(X) = \dfrac{1}{2}\displaystyle\sum_{i \neq j} V_\varepsilon(|x_j - x_i|)$ for every finite $X = \{x_j\} \subset \mathbb{R}^2$.

Variable: $X \leftrightsquigarrow \mu := \sum_{x_i \in X} \delta_{x_i}$.

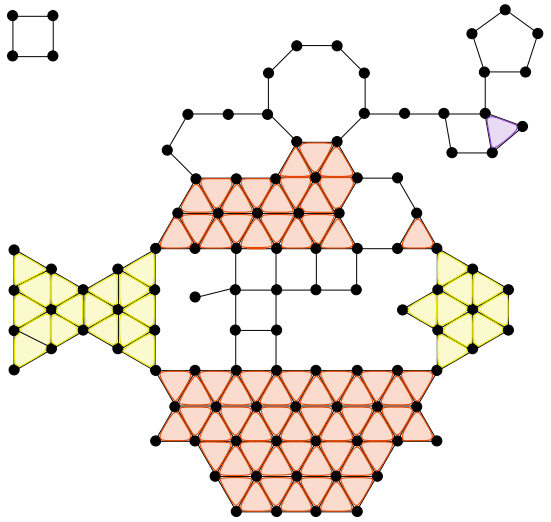
Quasiminimizers: $\varepsilon\big(\mathcal{E}_\varepsilon^{\mathrm{HR}}(\mu) + 3\mu(\mathbb{R}^2)\big) \leq C$.

Local orientation

Local orientation:

$T_\varepsilon \in F_\varepsilon^{\triangle}(X) \rightsquigarrow \theta(T_\varepsilon)$. We set

$$\theta_\varepsilon(\mu) := \sum_{T_\varepsilon \in F_\varepsilon^{\triangle}(X)} \theta(T_\varepsilon)\chi_{T_\varepsilon}.$$



Theorem (De Luca, Novaga, P., 2019)

Let $\mathcal{E}_\varepsilon^{\mathrm{HR}}(\mu_\varepsilon) + 3\mu_\varepsilon(\mathbb{R}^2) \leq \frac{C}{\varepsilon}$. *Then, up to a subsequence,* $\theta_\varepsilon(\mu_\varepsilon) \rightharpoonup \theta$ *in* $SBV_{\mathrm{loc}}(\mathbb{R}^2)$, *for some* $\theta = \sum_{j\in J} \theta_j \chi_{\omega_j}$ *in* $SBV(\mathbb{R}^2)$, *where* $\{\omega_j\}_j$ *is a Caccioppoli partition of a set of finite perimeter* Ω.

Ω = polycrystal

ω_j = grains of the polycrystal Ω

The effective energy for single crystals

$\varepsilon(\mathcal{E}_\varepsilon^{\mathrm{HR}}(\mu_\varepsilon) + 3\mu_\varepsilon(\mathbb{R}^2)) \overset{?}{\to} \mathcal{E}$ for some functional $\mathcal{E}$ as $\varepsilon \to 0$?

We answer to this question when $\theta_\varepsilon(\mu_\varepsilon) \rightharpoonup \theta = \bar{\theta}\chi_\Omega$ for some $\bar{\theta}$.

The effective energy $\mathcal{E}$ is the crystalline perimeter $\mathrm{Per}_{\varphi_{\bar{\theta}}}$ associated to $\bar{\theta}$:

The corresponding Wulff shape is the regular hexagon "oriented according with $\bar{\theta}$".

Theorem (De Luca, Novaga, P., 2019)

The following Γ-convergence result holds true.

(i) *(Γ-liminf inequality) Let $\{\mu_\varepsilon\}$ satisfy (a) and (b) with $\theta \equiv \bar{\theta}\chi_\Omega$. Then*

$$\liminf_{\varepsilon\to 0} \varepsilon(\mathcal{E}_\varepsilon^{\mathrm{HR}}(\mu_\varepsilon) + 3\,\mu_\varepsilon(\mathbb{R}^2)) \geq \mathit{Per}_{\varphi_{\bar{\theta}}}(\Omega)\,.$$

(ii) *(Γ-limsup inequality) For every set $\Omega \subset \mathbb{R}^2$ of finite perimeter and for every $\bar{\theta} \in (\frac{\pi}{3}, \frac{2}{3}\pi]$, there exists $\{\mu_\varepsilon\}$ satisfying (a) and (b) with $\theta = \bar{\theta}\chi_\Omega$ such that*

$$\limsup_{\varepsilon\to 0} \varepsilon(\mathcal{E}_\varepsilon^{\mathrm{HR}}(\mu_\varepsilon) + 3\,\mu_\varepsilon(\mathbb{R}^2)) \leq \mathit{Per}_{\varphi_{\bar{\theta}}}(\Omega)\,.$$

Friedrich-Kreutz-Schmidt, 2020: Γ-convergence analysis for polycrystals.

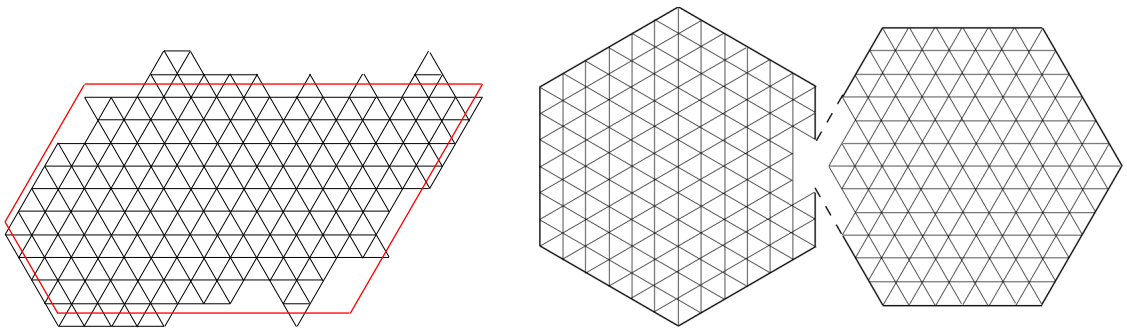
Single crystals vs polycrystals

Minimal energy among empirical measures converging to Ω:

$$\inf_{\varepsilon^2 \frac{\sqrt{3}}{2} \mu_\varepsilon \overset{\star}{\rightharpoonup} \chi_\Omega \, \mathrm{d}x} \liminf_{\varepsilon \to 0} \varepsilon(\mathcal{E}_\varepsilon^{\mathrm{HR}}(\mu_\varepsilon) + 3\mu_\varepsilon(\mathbb{R}^2))$$

Note: Depending on the shape of Ω,

both single crystals and polycrystals could be energetically convenient!



Comment: We have

$$\liminf_{\varepsilon \to 0} \varepsilon(\mathcal{E}_\varepsilon^{\mathrm{HR}}(\mu_\varepsilon) + 3\,\mu_\varepsilon(\mathbb{R}^2)) \geq \mathcal{H}^1(\partial^*\Omega) + \frac{1}{2}\mathcal{H}^1(\cup_j \partial^*\omega_j \setminus \partial^*\Omega)\,.$$

In contrast with Read-Shockley formula, 1950: gb energy density $\sim |[\theta]| \log |[\theta]|$

$\rightsquigarrow$ too rigid potential (no elasticity, no dislocations).

Open problem: Consider elastic potentials.

A plenty of potentials, ground states and Wulff shapes

Square lattices: If the well of the potential is large enough the square lattice is energetically better than the triangular one (Bétermin - De Luca - Petrache 2021).

Potentials with heavy tail (Kubin - P., 2021): Consider hard d-spheres interacting with an attractive pairwise potential $K^p(r) \sim -\frac{1}{r^p}$ for large r, with $p \in (0, d+1)$.

- For $0 < p < d$

$$K_\varepsilon^p(r) := \begin{cases} +\infty & \text{for } r \in [0, 2\varepsilon)\,, \\ -\dfrac{1}{r^p} & \text{for } r \in [2\varepsilon, \infty)\,. \end{cases}$$

  The Γ-limit is a nonlocal energy

$$E(\Omega) = -\int_\Omega \int_\Omega \frac{1}{|x-y|^p}\, dx\, dy;$$

- For $d \le p = d + s < d + 1$

$$K_\varepsilon^{d+s}(r) := \begin{cases} +\infty & \text{for } r \in [0, 2\varepsilon)\,, \\ 0 & \text{for } r \in [2\varepsilon, r_\varepsilon)\,, \\ -\frac{1}{r^{d+s}} & \text{for } r \in [r_\varepsilon, +\infty)\,. \end{cases}$$

  The Γ-limit is the s-fractional perimeter of Ω.

$$P^s(\Omega) = \int_\Omega \int_{\Omega^c} \frac{1}{|x-y|^{d+s}}\, dx\, dy;$$

In both cases (either by Riesz inequality or by fractional isoperimetric inequalities) the Wulff shape is the Euclidean ball (Kubin - P., 2021)

A plenty of potentials, ground states and Wulff shapes

Remark For $s = 0$ we are dealing with a 0-fractional perimeter (De Luca - Novaga, P., 2020).

Questions: For $p \geq d + 1$? Some reults in De Luca - Kubin - P. 2021 suggest that the tail energy behaves like the Euclidean perimeter. Neglecting the core energy leads to round Wulff shapes?

$$K_\varepsilon^6(r) := \begin{cases} +\infty & \text{for } r \in [0, 2\varepsilon)\,, \\ 0 & \text{for } r \in [2\varepsilon, r_\varepsilon)\,, \\ -\frac{1}{r^6} & \text{for } r \in [r_\varepsilon, +\infty)\,. \end{cases}$$

What happens if we remove the mesoscale r_ε?

For the original Lennard-Jonnes potential? Some numerical evidence for the hexagon (Ben Haj - Yedder - Blanc-Le Bris, 2003).

Failure of crystallization

Generalized (p, q)-Lennard-Jones potentials also referred to as Mie potentials, defined as $LJ^{p,q}(r) := r^{-p} - r^{-q}$ $(q < p)$

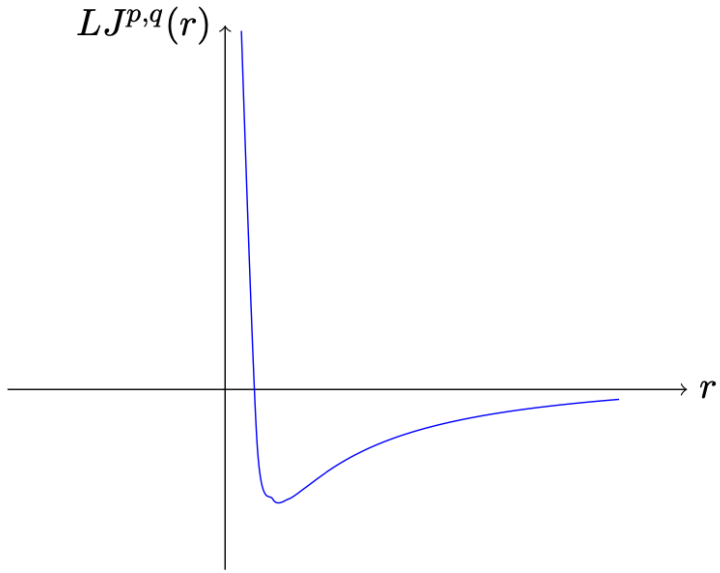


Figure 1. The function $r \to V(r)$

Non stable potential: We consider the one dimensional case $d = 1$, $0 < q < 1 < p$; $q < 1 \mapsto$ the potential is not stable: The energy per particle diverges as $N \to +\infty$! Consider a string of N equispaced particles and optimize with respect to the mutual distance:

Characteristic lengths:

Lattice spacing: $r_N := N^{\frac{q-1}{p-q}} \to 0$.

Length of the chain: $R_N := N^{\frac{p-1}{p-q}} \to +\infty$.

Γ-convergence analysis

The Γ-convergence analysis (Crismale-Kubin-Ninno-P. 2022) reveals that the density of the chain is not constant, being higher in the middle of the chain.

Scaled empirical measures: Let $R_N := N^{\frac{p-1}{p-q}}$.

$$\hat{\mu}_N(A) := \frac{1}{N}\mu_N\left(R_N A\right), \text{ for all borel set } A,$$

Γ-limit:

$$F(\mu) := \zeta(p)\int_{\mathbb{R}} f(x)^{p+1}\,dx - \frac{1}{2}\int_{\mathbb{R}}\int_{\mathbb{R}} \frac{1}{|x-y|^q} f(x)f(y)\,dx\,dy \qquad \text{for } \mu = f\mathcal{L}^1$$

Asymptotic behaviour of minimizers: Let μ_N be such that $E_N(\mu_N) - \inf E_N \to 0$. Then, up to a subsequence, there exists a sequence of translations $\{\tau_N\}$ such that $\hat{\mu}_N(\cdot - \tau_N) \xrightarrow{L} \mu(\cdot) \in \mathcal{M}_b(\mathbb{R})$. Moreover, μ is absolutely continuous and it is a minimizer of the functional F. Finally, any minimizer of F is not of the form $c\chi_I$.

In this respect, crystallization in any reasonable sense does not hold.

In fact, for N large enough, the density of a minimizer is not uniform (being in fact maximal in the middle of the chain).

Systems of oriented particles

For $N \in \mathbb{N}$ we consider configurations $(X_N, V_N) = \{(x_1, v_1), \dots, (x_N, v_N)\}$ with

$$x_j \in \mathbb{R}^2 \quad \leftrightsquigarrow \quad \text{position of the } j\text{-th particle}$$

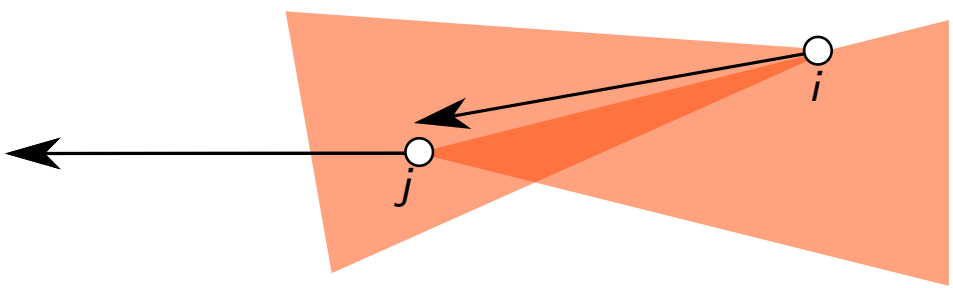
$$v_j \in \mathcal{S}^1 \quad \leftrightsquigarrow \quad \text{orientation of the } j\text{-th particle}$$

Vectorial crystallization problems. Basic problem: minimize pairwise interactions depending on both positions and orientations, with (possible) applications to crystallization of proteins and collective behaviour.

A simple variational model for fish schooling

Fishes: Rigid disks (Heitmann-Radin formalism).

Convenient interactions: "i follows j" $\leftrightsquigarrow$ j is in the *visual cone* of i and i is in the *wake cone* of j .



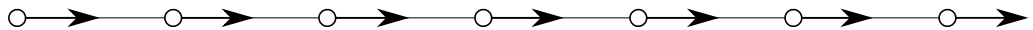
Assumption: visual and wake cones have the same amplitude 2ϑ .

School Efficiency: Maximize the number of convenient interactions;
Setting $\gamma := \cos\vartheta$, we have

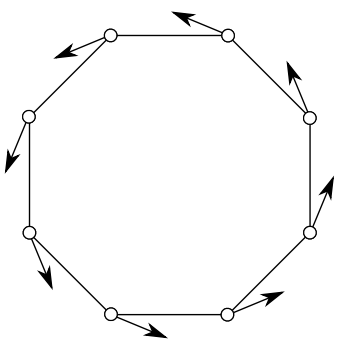
$$\mathcal{E}^\gamma(X, V) := -\sharp \text{ convenient interactions},$$

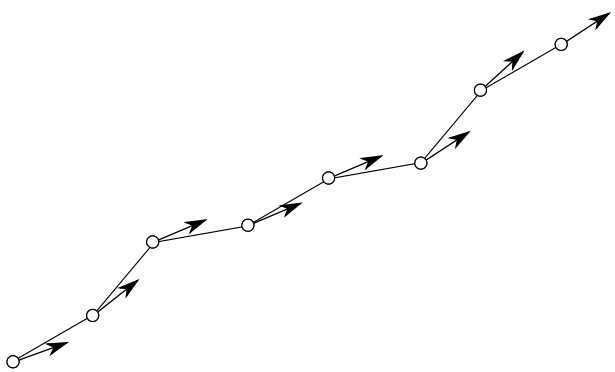
Some cases

- If $\gamma = 0$, same minimizers as in the Heitmann-Radin ($\triangle$ lattice)
- If $\gamma = 1$, minimizers are straight lines (duckling in a row)



- If $\frac{\sqrt{3}}{2} < \gamma < 1$, minimizers are

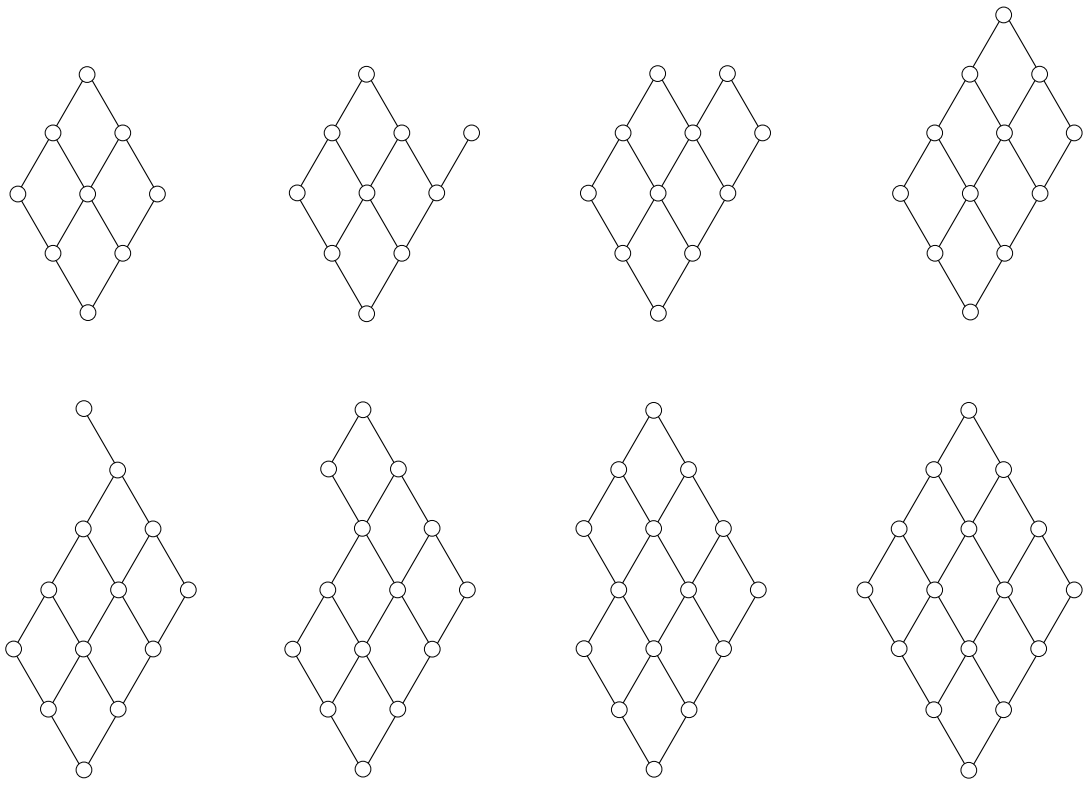




The case $\gamma = \frac{\sqrt{3}}{2}$: the diamond formation

Theorem (De Luca, Ninno, P., 2022)

The diamond configurations



are minimizers of the energy $\mathcal{E}^{\frac{\sqrt{3}}{2}}$.

Questions: Characterize all minimizers; the macroscopic shape of quasi-minimal schools; more general potentials (less rigid); true dynamical models; simulations.