Crystallization in the Wulff Shape via Gamma-Convergence

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1. Introduction

Aims:

- Do not start a priori from a lattice model, but allow arbitrary atomic positions.
- Justify, at zero temperature, why a large number of atoms self-assemble in crystalline order into a cluster of special geometric shape.
- Identify the cluster set.

It turns out that both points above are ultimately consequences of energy minimization at the atomistic level.

Key ingredients:

- Rigorous interfacial energy via Γ-convergence
- Wulff sets as minimizers of a coarse-grained Herring-type functional

2. Setting

Starting point:

- N atoms with centers at $x_i \in \mathbb{R}^2$
- interatomic short-range potential, $V: \mathbb{R}_{>0} \to \mathbb{R} \cup \{\infty\} =: \overline{\mathbb{R}}$, to be specified later,
- model potential energy

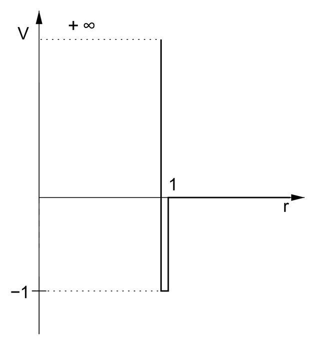
$$E: \mathbb{R}^{2N} \to \overline{\mathbb{R}}, \quad E(x_1, \ldots, x_N) := \frac{1}{2} \sum_{i \neq j} V(|x_i - x_j|).$$

Interatomic short-range potential:

Our analysis is carried out for the following potentials V:

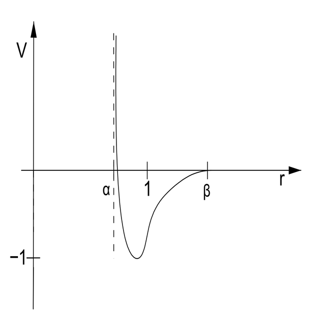
i. Heitmann-Radin 'sticky disc' potential

$$V(r) = \begin{cases} +\infty & 0 < r < 1 \\ -1 & r = 1 \\ 0 & r > 1 \end{cases}$$



ii. short-range pair-potential

$$V(r) = \begin{cases} +\infty & 0 < r < \alpha \\ \text{cts.} & \alpha \leq r \leq \beta \\ 0 & r \geq \beta, \end{cases}$$



(where: • minimum attained at $r = 1$,
• narrow well property fulfilled, i.e. α, β close to 1)

Essential ingredient:

Associate to each atomic configuration $\{x_1, \ldots, x_N\} \subset \mathbb{R}^2$ its re-scaled empirical measure

$$\mu_N := \frac{1}{N} \sum_{i=1}^{N} \delta_{x_i/\sqrt{N}} \tag{1}$$

Remarks.

- Re-scaling in (1) makes expected mass and volume of minimizing configuration bounded as N gets large.
- Usage of empirical measure and identification of limit measure via Gamma-convergence first introduced in [2].
- Empirical measure (Eulerian viewpoint) makes physically more sense here than a Lagrangian viewpoint in which one parametrizes an atomistic configuration by displacement from a reference configuration.

7. References

[1] Y. Au Yeung, G. Friesecke and B. Schmidt. Minimizing atomic configurations of short range pair potentials in two dimensions: crystallization in the Wulff shape, to appear in Calc. Var. and PDE.
[2] S. Capet, G. Friesecke. Minimum energy configurations of classical charges: Large N asymptotics. *Appl. Math. Research Express, doi:10.1093/amrx/abp002, 2009*
[3] I. Fonseca and S. Müller. A uniqueness proof for the wulff theorem. *Proc. R. Soc. of Edinburgh*, 119(1–2):125–136, 1991.
[4] R. C. Heitmann and C. Radin. The ground states for sticky disks. *Journal of Statistical Physics*, 22(3):281–287, 1980.
[5] J. E. Taylor. Unique structure of solutions to a class of nonelliptic variational problems. *Proc. Symp. in Pure Mathematics*, 27:419–427, 1974.

3. Formation of Cluster

Theorem 1. (Compactness and Formation of cluster, [1])
Let V be an interatomic short-range potential (see ii.), $\{x_1^{(N)}, \ldots, x_N^{(N)}\}$ be a sequence of connected N-particle configurations of bounded surface energy,

$$E(x_1^{(N)}, \ldots, x_N^{(N)}) \leq -6N + CN^{1/2}, \tag{2}$$

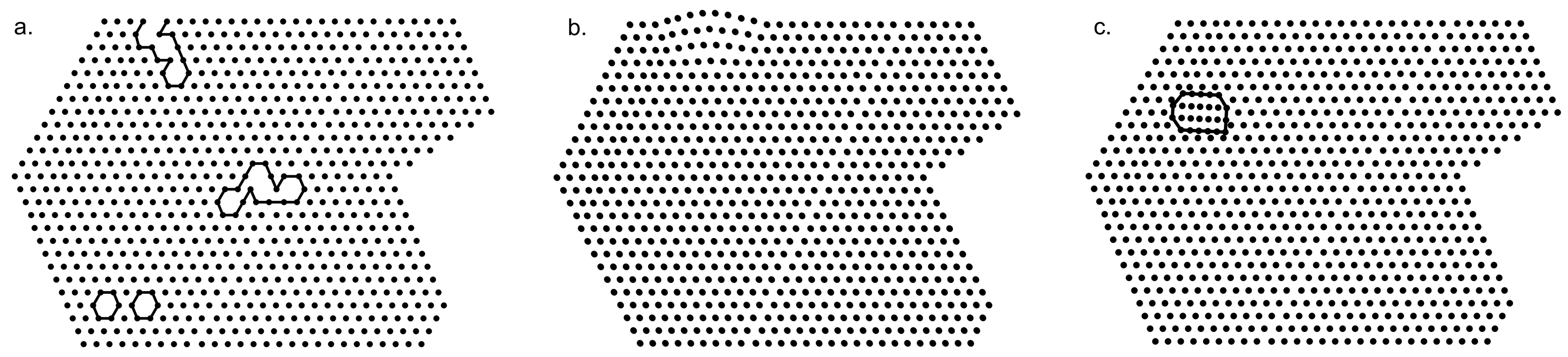
and μ_N be its re-scaled empirical measures (see (1)). As $N \to \infty$, up to subsequences,

$$\mu_N \rightharpoonup^* \frac{2}{\sqrt{3}} \chi_E,$$

where E is a set of finite perimeter of volume $\frac{\sqrt{3}}{2}$.

Remarks.

- In fact, any set E of finite perimeter and volume $\frac{\sqrt{3}}{2}$ can arise.
- Configurations containing (a.) vacancies, (b.) elastic deformations or (c.) inclusions of phases with different lattice structures satisfy the bounded surface energy condition (2), and in particular the hypotheses of Theorem 1, as long as these only occupy regions of size $O(N^{1/4})$.



4. Wulff Shape, Identification of Cluster

Theorem 2. (Wulff shape, [1])
Let V be the Heitmann-Radin potential (see i.), $\{x_1^{(N)}, \ldots, x_N^{(N)}\}$ be a sequence of minimizers of E and let μ_N be its associated re-scaled empirical measure (cf. (1)). Then

- (Heitmann/Radin 1980, [4]) up to a rigid transformation $\{x_1^{(N)}, \ldots, x_N^{(N)}\}$ is a subset of the triangular lattice,
- as $N \to \infty$, up to subsequences and rigid transformation,

$$\mu_N \rightharpoonup^* \frac{2}{\sqrt{3}} \chi_H, \qquad \text{where } H \text{ is a regular hexagon.}$$

5. Rigorous Interfacial Energy Result

It is convenient to re-write E in terms of the re-scaled empirical measure, introduced in (1):

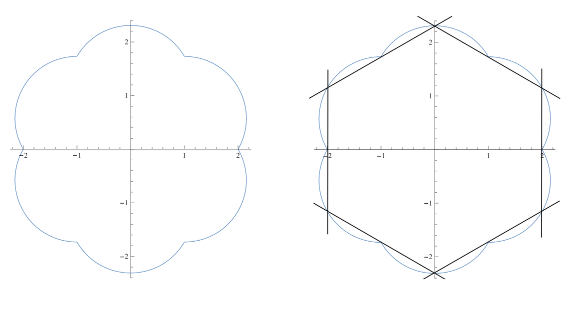
$$I_N(\mu) := \begin{cases} E(x_1, \ldots, x_N), & \mu = \frac{1}{N} \sum_{i=1}^{N} \delta_{x_i/\sqrt{N}}, \ x_i \text{ distinct on triangular lattice} \\ +\infty, & \text{otherwise} \end{cases}$$

Theorem 3. (Interfacial energy result, [1])
The sequence $N^{-1/2}(I_N - \inf I_N)$ converges in the sense of Gamma-convergence to the Wulff/Herring type functional

$$I_\infty(\mu) := \begin{cases} \int_{\partial^* E} \Gamma(\nu_E)\, d\mathcal{H}^1(x), & \mu = \frac{2}{\sqrt{3}} \chi_E \text{ for some set E of finite perimeter and mass } \frac{\sqrt{3}}{2} \\ +\infty, & \text{otherwise,} \end{cases}$$

w.r.t. weak$\star$ convergence of probability measures. Γ is the surface energy density and can be calculated explicitly.

Remark. The limiting cluster set in Theorem 2, a regular hexagon, can be identified by observing that I_∞ is, up to translation, uniquely minimized by the characteristic function of the Wulff set (cf. [3],[5]).



On the left is the polar plot of Γ; on the right is the Wulff set obtained as the intersection of the highlighted hyperplanes

6. Offshot and Ongoing Work

Our prototype model already captures the key aspects of (1) formation of a local lattice structure, (2) emergence of a well-defined surface energy density (as N becomes large) and (3) the emergence of an overall geometric Wulff shape.

Ongoing work:
generalizations to 3D, in particular establishing the rigorous Gamma-limit for several lattices, e.g. fcc and hcp, and identification of the limiting Wulff shapes.