

The Problem of crystallization

Crystallization is a natural process in which atoms or molecules arrange themselves in a periodic pattern to form solids. Mathematically we would like to understand why such formations are favorable. This is usually formulated by a minimization problem where mostly nearest-neighbor interactions are considered.

Graphene

Graphene is a form of carbon, where the atoms are arranged on a hexagonal lattice which forms a single layer or 2D-material.

Polycrystals

A Polycrystal is a solid that consists of multiple crystallites of varying size and orientation. Each crystallite (or equivalently grain) is a highly ordered arrangement of atoms on a specific periodic pattern (lattice).

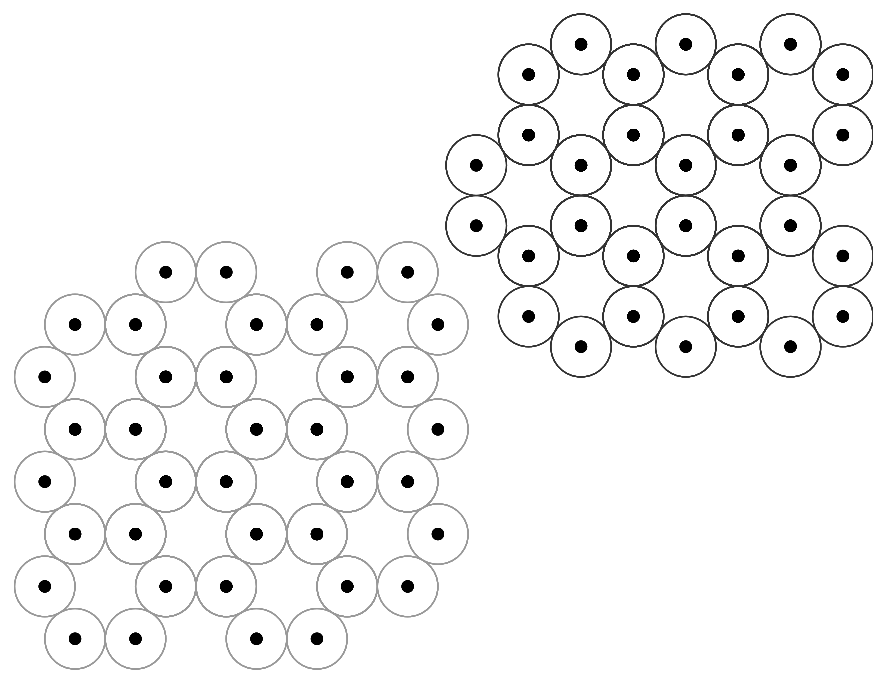


Fig. 1: This shows a polycrystal consisting of two grains. Here the atoms are modelled as hard spheres.

Crystallization in Carbon Nanostructures

The paper 'Crystallization in Carbon Nanostructures' by Mainini and Stefanelli considered a class of energies of the form (including the case $\tilde{V}_2 = V_2, \tilde{V}_3 = V_3$)

$$\mathcal{E}(X) = \frac{1}{2} \sum_{i \neq j} \tilde{V}_2(|x_i - x_j|) + \frac{1}{2} \sum_A \tilde{V}_3(\theta_{ijk}),$$

where $X = \{x_k\}_{k=1}^N$ and A denotes the active bonds of length 1. They showed that configurations under the constraint $\#X = N$, where $N \in \mathbb{N}$ is fixed, are subsets of a hexagonal lattice and that it holds

$$\min\{\mathcal{E}(X) \mid \#X = N\} = -\left[\frac{3}{2}N - \sqrt{\frac{3}{2}N}\right].$$

Embedding of configurations

To derive an effective limit theory it was crucial to choose an embedding, which keeps the main features of configurations and their energy. For this we associate to a configuration X a function $u \in PC(\mathbb{R}^2; \mathcal{Z})$, where $PC(\mathbb{R}^2; \mathcal{Z})$ is the space of piecewise constant functions with values in \mathcal{Z} . Here $z \in \mathcal{Z}$ corresponds to a specific translation and rotation of the 'base' hexagonal lattice

$$\mathcal{L}_0 := \left\{ p \begin{pmatrix} 0 \\ \sqrt{3} \end{pmatrix} + q \begin{pmatrix} \frac{3}{2} \\ \frac{\sqrt{3}}{2} \end{pmatrix} + \delta \begin{pmatrix} 1 \\ 0 \end{pmatrix} \mid p, q \in \mathbb{Z}, \delta \in \{\pm 1\} \right\}.$$

The grains then correspond to the regions G_j where the function has a constant value. Each grain is made up of a union of Voronoi cells of points $x \in X$ with perfect configuration, i.e.

$$\begin{aligned} \#\mathcal{N}_\varepsilon(x) &= 3, \\ \theta_{yxz} &\equiv 0 \pmod{\frac{2\pi}{3}} \quad \forall y, z \in \mathcal{N}_\varepsilon(x), y \neq z. \end{aligned}$$

This embedding allows us to use the theories of BV-functions and Γ -convergence.

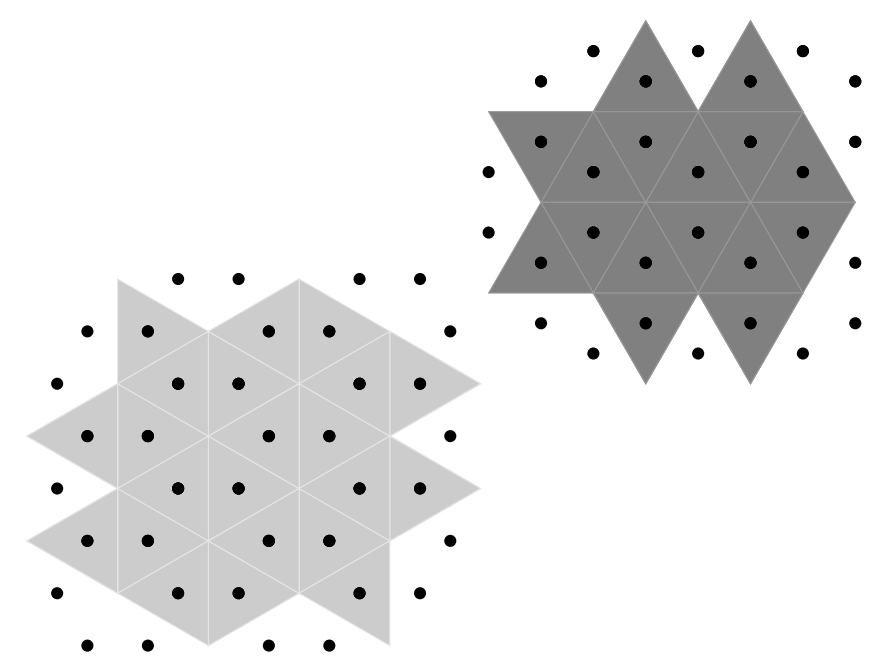


Fig. 2: This shows the relation of a configuration X and its function u . Here the regions in different shades of grey indicate regions where $u = z$. As one can see, they are made up of the respective Voronoi cells, i.e. each region is a union of equilateral triangles.

Compactness

Theorem

Let $\{X_\varepsilon\}_\varepsilon$ be a sequence of configurations with

$$\sup_{\varepsilon > 0} E_\varepsilon(X_\varepsilon) < \infty$$

Then there exists a subsequence $\{\varepsilon_k\}_{k \in \mathbb{N}}$ with $\varepsilon_k \rightarrow 0$ as $k \rightarrow \infty$ and a function $u \in PC(\mathbb{R}^2; \mathcal{Z})$ such that $X_{\varepsilon_k} \rightarrow u$ in $L^1_{loc}(\mathbb{R}^2)$ as $k \rightarrow \infty$.

The mathematical model

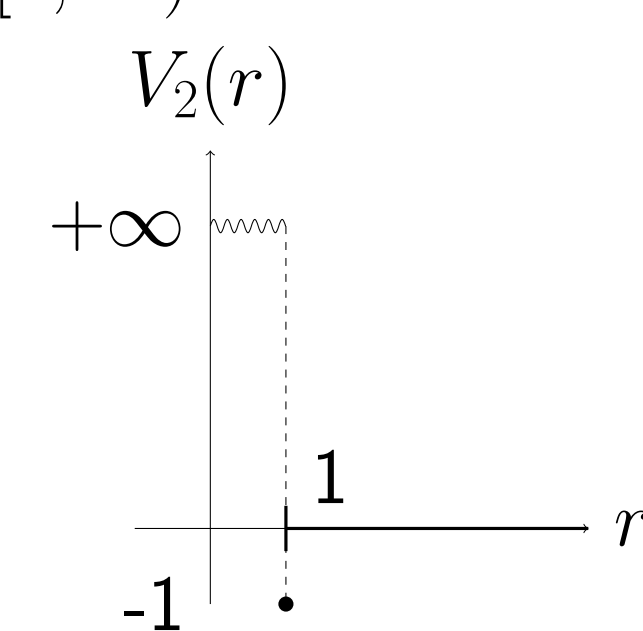
In order to study the behaviour of graphene polycrystals, we model a configuration X of atoms as a subset of \mathbb{R}^2 in which each atom $x \in X$ can be thought of as a hard sphere of a fixed diameter $\varepsilon > 0$ (This coincides with the lattice spacing). We consider a family of configurational energies $E_\varepsilon(X)$ consisting of two and three body interaction terms.

Two body term

The two body term models the atoms as spheres that cannot intersect on a finite energy scale and experience attractive forces up to an equilibrium distance exactly when the spheres are tangential. For an atom $x \in X$ we define its ε -neighbors

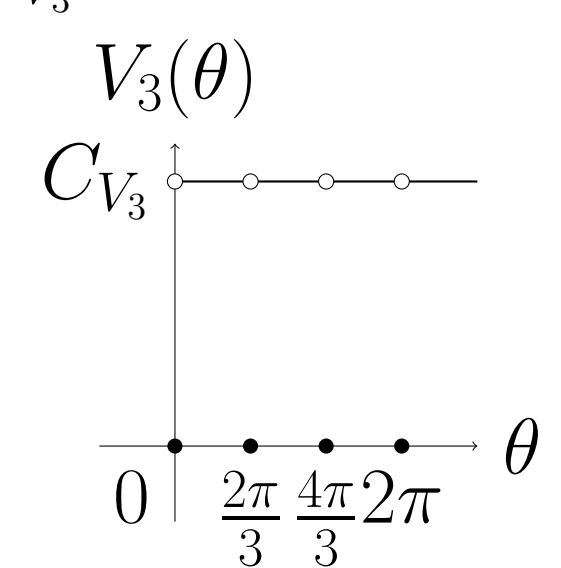
$$\mathcal{N}_\varepsilon(x) := \{y \in X \mid |x - y| = \varepsilon\}.$$

The two body term is then given by the Heitmann-Radin Sticky Disk potential $V_2 : [0, \infty) \rightarrow \mathbb{R}$



Three body term

The three body term accounts for the angle spanned by an atom and two of its nearest neighbors. Thus an energy contribution via the three body or angle term can only occur for so called active bonds of length ε , i.e. triples (x, y, z) where $x, y, z \in X$ and $|x - y| = |y - z| = \varepsilon$. To such a triple we associate the angle θ_{xyz} spanned between the vectors $x - y$ and $z - y$. The angle term is then given by $V_3 : [0, 2\pi] \rightarrow \mathbb{R}$ with a constant $C_{V_3} > 0$



Configurational energy

In order to pass from a discrete model to a continuum model, we want to consider $\varepsilon \rightarrow 0$, where $\varepsilon > 0$ is the lattice spacing. This is done by a renormalization which removes the cardinality constraint by subtracting the minimal energy of $-\frac{3}{2}$ per particle and rescale by the diameter of a N -particle configuration X_N , which is $\sim \sqrt{N}$, i.e. we look at

$$\frac{\mathcal{E}(X_N) + \frac{3}{2}N}{\sqrt{N}}.$$

By setting $\varepsilon := \frac{1}{\sqrt{N}}$ and $X_\varepsilon := \varepsilon X_N$ and taking our potentials into consideration, the above term can be rewritten as

$$E_\varepsilon(X_\varepsilon) = \frac{1}{2} \sum_{x \in X_\varepsilon} \varepsilon \left(3 - \#\mathcal{N}_\varepsilon(x) + \sum_{y, z \in \mathcal{N}_\varepsilon(x), y \neq z} V_3(\theta_{yxz}) \right).$$

Γ -Convergence

We introduce the notion of convergence for a sequence of configurations $\{X_\varepsilon\}_\varepsilon$. We say that $X_\varepsilon \rightarrow u$ in $L^1_{loc}(\mathbb{R}^2)$ if the functions u_ε corresponding to X_ε satisfy $u_\varepsilon \rightarrow u$ in $L^1_{loc}(\mathbb{R}^2)$.

Theorem

It holds that $E = \Gamma(L^1_{loc})\text{-}\lim_{\varepsilon \rightarrow 0} E_\varepsilon$. More precisely we have

Γ -lim inf inequality: For each $u \in PC(\mathbb{R}^2; \mathcal{Z})$ and each sequence $\{X_\varepsilon\}_\varepsilon$ with $X_\varepsilon \rightarrow_{\varepsilon \rightarrow 0} u$ in $L^1_{loc}(\mathbb{R}^2)$ it holds that

$$\liminf_{\varepsilon \rightarrow 0} E_\varepsilon(X_\varepsilon) \geq E(u).$$

Γ -lim sup inequality: For each $u \in PC(\mathbb{R}^2; \mathcal{Z})$ there exists a sequence of configurations $\{X_\varepsilon\}_\varepsilon$ such that $X_\varepsilon \rightarrow_{\varepsilon \rightarrow 0} u$ in $L^1_{loc}(\mathbb{R}^2)$ and

$$\lim_{\varepsilon \rightarrow 0} E_\varepsilon(X_\varepsilon) = E(u).$$

Here the limiting functional $E : PC(\mathbb{R}^2; \mathcal{Z}) \rightarrow [0, \infty)$ is defined by

$$E(u) := \int_{J_u} \varphi(u^+(x), u^-(x), \nu_u(x)) d\mathcal{H}^1(x),$$

where J_u denotes the jump set of u . The density $\varphi : \mathcal{Z} \times \mathcal{Z} \times \mathbb{S}^1 \rightarrow [0, \infty)$ is given by the following

Proposition

For every $z^+, z^- \in \mathcal{Z}, \nu \in \mathbb{S}^1, x_0 \in \mathbb{R}^2$ and $\rho > 0$ there exists

$$\varphi(z^+, z^-, \nu) = \lim_{\varepsilon \rightarrow 0} \frac{1}{\rho} \min \{ E_\varepsilon(X, Q_\rho^\nu(x_0)) \mid X = \varepsilon \mathcal{L}(z^\pm) \text{ on } \partial_\varepsilon^\pm Q_\rho^\nu(x_0) \}$$

and is independent of x_0 and ρ .

The condition $X = \varepsilon \mathcal{L}(z^\pm)$ on $\partial_\varepsilon^\pm Q_\rho^\nu(x_0)$ imposes the fixed values z^\pm on a specific ε -boundary region of the upper and lower half of the cube $Q_\rho^\nu(x_0)$ with sidelength ρ , sides parallel to ν and center x_0 .