Graphene Polycrystals
A discrete to continuum limit
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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 \( V_2 = V_1 \leq V_3 \)).

\[
\mathcal{E}(\mathbf{X}) = \frac{1}{2} \sum_{j \in Z} \mathcal{V}(|x_j| - |x_0|) + \frac{1}{2} \sum_{i \in A} \mathcal{V}(\rho_0, \theta).
\]

where \( X = \{x_j\}_{j=1}^N \) and \( A \) denotes the active bonds of length \( l \). 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

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

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 \( u \in \text{PC}(R^2, Z) \), where \( \text{PC}(R^2, Z) \) is the space of piecewise constant functions with values in \( Z \). Here \( z \in Z \) corresponds to a specific translation and rotation of the ‘base’ hexagonal lattice

\[
\mathcal{L}_3 := \left\{ p \left( \frac{\theta}{\sqrt{3}} \right) + q \left( \frac{\phi}{\sqrt{3}} \right) \right\} \bigcup \left\{ p, q \in \mathbb{Z} \mid \theta, \phi \in \{ \pm 1 \} \right\}.
\]

The grains then correspond to the regions \( G_t \), 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.

\[
\# X_t(x) = 3, \quad \theta_{x,t} \equiv 0 \quad \text{mod } 2\pi \quad \forall y, z \in X_t(x), y \neq z.
\]

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

Fig. 2: This shows the relation of a configuration \( X \) and the function \( u \). Here the regions in different shades of grey indicate regions where \( \mu = 1 \). As one can see, they are made up of the respective Voronoi cells, i.e., each region is a union of equilateral triangles.

Compactness
Let \( \{X_k\} \) be a sequence of configurations with \( \sup_k \mathcal{E}(X_k) < \infty \). Then there exists a subsequence \( \{x_k\} \) converging to \( X_k \) as \( k \to \infty \).

The mathematical model
In order to study the behaviour of graphene polycrystals, we model a configuration \( X \) of atoms as a subset of \( R^2 \) 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 neighbors

\[
N(x) := \{ y \in X \mid |x - y| = \varepsilon \}.
\]

The two body term is then given by the Heitmann-Radin Sticky Disk potential

\[
\mathcal{V}_2(r) \to \mathbb{R}^2, \quad r \to \infty
\]

\[
\mathcal{V}_2(r) = \begin{cases} +\infty & \text{if } r < \varepsilon \\ 0 & \text{if } r = \varepsilon \\ -1 & \text{if } r > \varepsilon \end{cases}
\]

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 \( \varepsilon \), i.e., triples \( (x, y, z) \) where \( x, y, z \in X \) and \( |y - z| = |y - x| = \varepsilon \). To such a triple we associated the angle \( \theta_{x,y} \) spanned between the vectors \( x - y \) and \( y - z \). The angle term is then given by \( V_3 : \mathbb{R}^2 \to \mathbb{R} \) with a constant \( C_3 > 0 \).

\[
E_\varepsilon(X) = \frac{1}{2} \sum_{x \in X} \left( 3 - \# N(x) + \sum_{y \neq x \in N(x)} \mathcal{V}(\theta_{x,y}) \right).
\]

Configurational energy
In order to pass from a discrete model to a continuum model, we want to consider \( \varepsilon \to 0 \), where \( \varepsilon > 0 \) is the lattice spacing. This is done by a renormalization which removes the cardinality constraint by subtracting the minimal energy of \( -\frac{1}{2} \) per particle and rescale by the diameter of a \( N \)-particle configuration \( X_N \), which is \( \sqrt{N} \), i.e. we look at

\[
\mathcal{E}(\frac{X_n}{\sqrt{N}}) \to \mathbb{R}^2
\]

By setting \( \varepsilon := \frac{C_3}{N} \) and \( X_N := \varepsilon X_N \), and taking their potentials into consideration, the above term can be rewritten as

\[
E_n(X) = \frac{1}{\varepsilon^2} \sum_{x \in X} \left( 3 - \# N(x) + \sum_{y \neq x \in N(x)} \mathcal{V}(\theta_{x,y}) \right).
\]

Gamma-Convexence
We introduce the notion of convergence for a sequence of configurations \( \{X_k\} \). We say that \( X_k \to u \) in \( L^2_{\text{loc}}(R^2) \) if the functions \( u_k \) corresponding to \( X_k \) satisfy \( u_k \to u \) in \( L^2_{\text{loc}}(R^2) \).

Theorem
It holds that

\[
E = \Gamma(\liminf_{k \to \infty} E_{X_k}) \geq E(u).
\]

More precisely we have

\[
\Gamma\text{-lim inf inequality: For each } u \in \text{PC}(R^2, Z) \text{ and each sequence } \{X_k\}, \text{ with } X_k \to u \text{ in } L^2_{\text{loc}}(R^2) \text{ it holds that}
\]

\[
\liminf_{k \to \infty} E_{X_k} \geq E(u)
\]

\[
\Gamma\text{-lim sup inequality: For each } u \in \text{PC}(R^2, Z) \text{ there exists a sequence of configurations } \{X_k\}, \text{ such that } X_k \to u \text{ in } L^2_{\text{loc}}(R^2) \text{ and}
\]

\[
\limsup_{k \to \infty} E_{X_k} \geq E(u).
\]

Here the limiting functional \( E : \text{PC}(R^2, Z) \to [0, \infty) \) is defined by

\[
E(u) := \int_J \rho(z) dH(z)
\]

where \( J \) denotes the jump set of \( u \). The density \( \rho : Z \times Z \times S^1 \to [0, \infty) \) is given by the following

Proposition
For every \( z^+ \in Z \) \( z^- \in Z \), \( \rho^+ \in \mathbb{R}^2 \) and \( \rho^- \in \mathbb{R}^2 \) there exists

\[
\rho(z^+, \rho^+, \rho^-) := \lim_{r \to 0} \min_{\phi \in \mathbb{R}} \left\{ E_{\varepsilon}(X, Q_{\varepsilon}(x)) \mid X = \varepsilon Q_{\varepsilon}(x) \right. \text{ on } \partial^+ \mathbb{R}^2 \text{ and}
\]

\[
\left. \text{is independent of } x \text{ and } \rho \right\}
\]

The condition \( X = \varepsilon Q_{\varepsilon}(x) \) on \( \partial^+ \mathbb{R}^2 \) imposes the fixed variables \( z^+ \) on a specific boundary condition of the upper and lower half of the cube \( Q_{\varepsilon}(x) \) with side length \( \varepsilon \), sides parallel to \( \nu \) and center \( x_0 \).