Atomistic Models, Surface Energy and Wulff Shape in the Plane

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Chair of Analysis

Abstract

The majority of solid bodies turns out to be crystals or to have crystalline shapes making the research of crystals a serious matter for a vast field of sciences. From the microscopic point of view a crystal can be described as a periodic arrangement of a large number of atoms, ions or molecules, whereas from the macroscopic point of view a crystal is meant as an arrangement of many atoms that make up a "nice" geometric shape, namely the shape which is obtained by the celebrated Wulff construction.
Both interpretations have been observed in experiments hitherto. However, these two approaches are completely different and the problem of finding the connections between them remains until today a mathematical challenge.

Microscopic Approach

Model

We consider a system $\mathcal{S}_N = \{x_1, \ldots, x_N\} \subset \mathbb{R}^2$ containing $N \in \mathbb{N}$ non-overlapping atoms in $\mathbb{R}^2$ of unit diameter which are represented by their centers, i.e.

$$(1) \qquad \mathcal{S}_N \in \{A \subset \mathbb{R}^2 \mid \sharp A = N,\ \forall x \in A\, \forall y \in A \backslash \{x\} :\ |x-y| \geq 1\} =: \mathcal{A}.$$

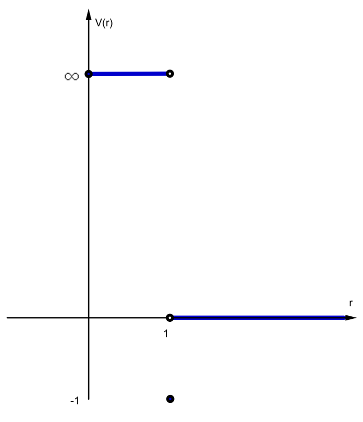
The pair-interaction between two atoms is modelled by a potential $V : \mathbb{R}_{\geq 0} \to \overline{\mathbb{R}}$ and the total potential energy of $\mathcal{S}_N$ is assumed to be

$$E(\mathcal{S}_N) := \sum_{i \leq i < j \leq N} V(|x_i - x_j|).$$

The configuration $\mathcal{S}_N$ is said to be *stable* or a *microscopic ground state* if it minimizes the potential energy E among all sets $S \in \mathcal{A}$.

Experimental observations lead to the conclusion that the *Lennard-Jones potential* defined by $\mathbb{R}_{\geq 0} \to \mathbb{R},\ r \mapsto r^{-12} - r^{-6}$ can be taken as a model pair-potential energy. However, for the sake of simplicity, we restrict our investigations to the so-called *sticky potential*, which is defined as follows

$$(2) \qquad V : \mathbb{R}_{\geq 0} \to \mathbb{R}, \qquad V(r) := \begin{cases} +\infty, & 0 \leq r < 1, \\ -1, & r = 1 \\ 0, & r > 1. \end{cases}$$



Graph of sticky potential

Result

R. C. Heitmann & C. Radin established in [4] the following theorem about the periodic arrangement of microscopic ground states.

Theorem 1. *(R. C. Heitmann & C. Radin, 1979)*
Let $N \in \mathbb{N}, N \geq 3$ and let $\mathcal{A}$ be defined as in (1). Moreover, we assume that the sticky potential is the underlying pair-interaction potential. Then there exists up to translation and rotation exactly one microscopic ground state which is a subset of $\mathcal{L}$, where

$$\mathcal{L} := \frac{1}{2}\begin{pmatrix} 2 & 1 \\ 0 & \sqrt{3} \end{pmatrix} \mathbb{Z}^2.$$

Macroscopic Approach

Model

The main interest in the macroscopic approach is to predict the equilibrium shape of a crystal. According to C. Herring's proposal (cf. [5]) the shape of a "very small" crystal can be obtained by minimizing the surface free energy among all sets of a given volume fully neglecting the interatomic forces. Here the given volume represents the occupied volume by a body $\Omega \subset \mathbb{R}^N$. Such a shape is called a (macroscopic) ground state.
To be more precise, let $\Gamma : S^{N-1} \to \mathbb{R}$ be the specific anisotropic surface free energy of a body with volume $meas(\Omega)$. Further assume that Γ is continuous and bounded away from zero. Then solutions of

$$(3) \qquad \min_{E \subset \mathbb{R}^N \text{ measurable with finite perimeter}} \int_{\partial^\star E} \Gamma(n_E(x))\, dH_{N-1}(x)$$

subject to $meas(E) = meas(\Omega)$ are called macroscopic ground states. As usual, $\partial^\star E$ is the reduced boundary of E, $n_E(x)$ the outward unit normal at x and H_{N-1} denotes the $(N-1)$-dimensional Hausdorff measure.

Result

There have been many different proofs regarding the existence and uniqueness of macroscopic ground states among others by I. Fonseca in [2] (existence) and I. Fonseca & S. Müller in [3] (uniqueness).

Theorem 2. *(I. Fonseca, 1991)*
Under the given hypothesis the set

$$(4) \qquad W_\Gamma := \{x \in \mathbb{R}^N\ ;\ x \cdot n \leq \Gamma(n)\ \ \forall n \in S^{N-1}\}$$

is a macroscopic ground state, i.e. W_Γ solves (3) subject to the volume constraint $meas(E) = meas(W_\Gamma) = const.$

Theorem 3. *(I. Fonseca & S. Müller, 1991)*
Under the given hypothesis macroscopic ground states are unique in the following sense: if $E \subset \mathbb{R}^N$ is a measurable set of finite perimeter and a solution of (3), then $\|\chi_{E+c} - \chi_{W_\Gamma}\|_{L^1} = 0$, where χ denotes the characteristic function and

$$c := \frac{1}{meas(W_\Gamma)} \left(\int_{W_\Gamma} x\, dx - \int_E x\, dx \right).$$

Thus a macroscopic ground state is up to sets of measure zero and translation uniquely defined. The set W_Γ defined in (4) is called Wulff set (shape) or crystal of Γ.

Atomistic-to-Continuum limit

Goal

It would be desirable to justify the Wulff shape W_Γ in consequence of interatomic forces, i.e. as a minimizer of the total potential energy. In other words, one wants to prove that for $N \to \infty$ a microscopic ground state is also a macroscopic ground state.

Γ-Convergence

Our attempt is to establish the atomistic-to-continuum limit via Γ-convergence for a family of functionals which have their domains on the space of all non-negative Radon measures and to employ the weak$\star$-convergence therein.
For this purpose, we replace the model total potential energy $E(\mathcal{S}_N)$ for a configuration $\mathcal{S}_N = \{x_1, \ldots, x_N\} \in \mathcal{A}$ by a functional I_N on the space of all non-negative Radon measures defined by

$$I_N(\mu) := \begin{cases} +\infty, & \mu \neq \sum_{i=1}^N \delta_{x_i} \\ \frac{1}{2} \iint_{R^4 \backslash \text{diag}} V(|x-y|)\, d\mu \otimes d\mu, & otherwise, \end{cases}$$

where *diag* denotes the set $\{(x,x)^T \in \mathbb{R}^4\ ;\ x \in \mathbb{R}^2\}$.

Conjecture

I_N Γ-converges to a functional I. A minimizer of I is up to translation and rotation a characteristic function of the Wulff set.

References

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