3d Crystallization

FCC structures

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Outline

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Extremum principles

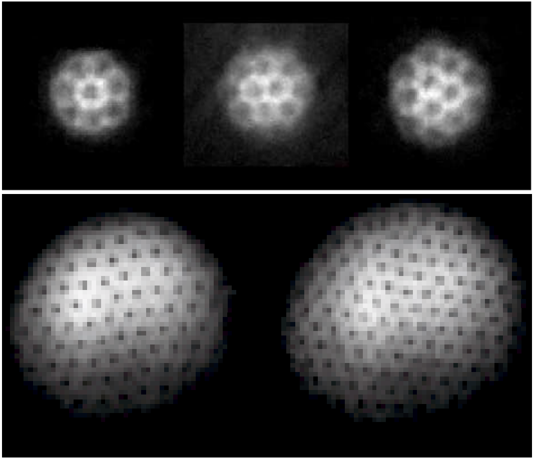
- Crystalline structure is the minimizer of the minimum of the electronic energy subject to fixed positions of the nuclei.
- Other examples: Vortex patterns in Bose-Einstein condensates, Abrikosov lattice, carbon nanotubes etc

Minimizers of the Gross-Pitaevskii functional:

$$E_{\mathrm{GP}}(\psi) = \frac{1}{2}\int_{\mathbb{R}^2} \left[|\nabla\psi - i\Omega \times r\psi|^2 + (1-\Omega^2)r^2|\psi|^2 + Na|\psi|^4 \right]$$

converge to the Abrikosov lattice as $\Omega \to (0,0,1)$.

Experimental pictures of the Abrikosov lattice



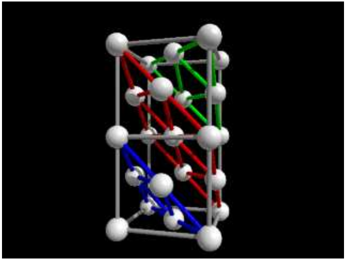
Outline

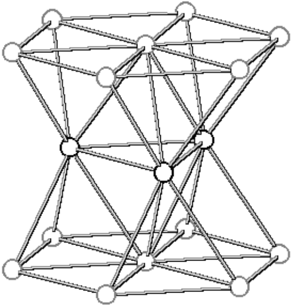
1. Motivation/Phenomena
   - Periodic minimizers
   - What is a Solid Phase?
   - Classical models
2. Our Contribution
   - Rigorous Results
   - Basic Ideas for Proofs

Crystals are the most common solids

230 (17) different space groups in 3d (2d).

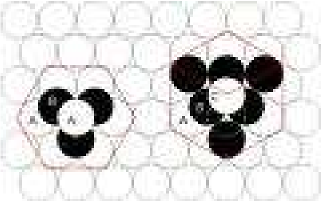
- Most common crystalline lattices are fcc (face-centered cubic), hcp (hexagonally close packed) and bcc (body centered cubic).
- Only fcc and hcp are close packings.





Multiplicity of close packings: Stacking sequence

- Many non-equivalent close packings can by constructed by stacking 2d triangular lattices.
- An hcp-lattice is obtained if the particles in the third layer are on top of the particles in the first layer.
- An fcc-lattice is obtained if the particles in the third layer are on top of the holes in the first and second layer. (ABABA... = hcp, ABCABC = fcc).
- Third-nearest neighbors are closer in the hcp-lattice.



First approach: Dense packings

- Kepler's letter from 1611 'Strena seu de Nive Sexangula' (A New Year's Gift of Hexagonal Snow) to his sponsor Johannes Matthias Wacker discusses the possibility that a regular packing of spherical particles is responsible for the hexagonal symmetry of snowflake crystals.
- Kepler rejects the atomic hypothesis and says that the particles might be some kind of vapor balls.
- He conjectures that the reason for the periodic arrangement is that the surface might impede expansion, like a pomegranate.
- In 2005 Thomas Hales published a rigorous proof of Kepler's conjecture (Ann. Math. 162 (3): 1065-1185).

Kissing problems

- Famous discussion between Isaac Newton and David Gregory (Savillian Professor of Geometry in Oxford) in 1694: Can 13 spheres touch a given sphere at the same time?
- Configurations with 12 spheres are *highly* degenerate.
- First proof: Schütte & van der Waerden (Math. Ann. 53, 325-334, 1953).

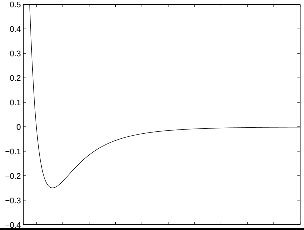
Outline

Two- and three-body energies

$$E_n(y) = \frac{1}{2} \sum_{\substack{1 \le i,j \le n \\ i \ne j}} V_2(|y_i - y_j|) + \frac{1}{6} \sum_{\substack{1 \le i,j,k \le n \\ i \ne j \ne k}} V_3(y_j - y_i, y_k - y_i)$$

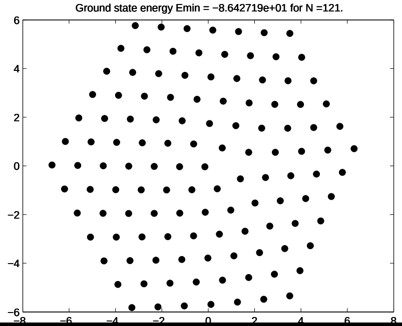
$y_i \in \mathbb{R}^d$, $i = 1 \ldots n$, $d \in \{1, 2, 3\}$ are the positions of n particles.

The Lennard-Jones potential $V_{\mathrm{LJ}}(r) = r^{-12} - r^{-6}$ accounts for van-der-Waals interactions at long distances.



Interesting equilibria in the Lennard-Jones case

- Simple evaluation $\rightarrow$ efficient simulation
- Finite temperature, phase transitions
- Interesting critical points: dislocations
- Unusual interaction between local and global phenomena



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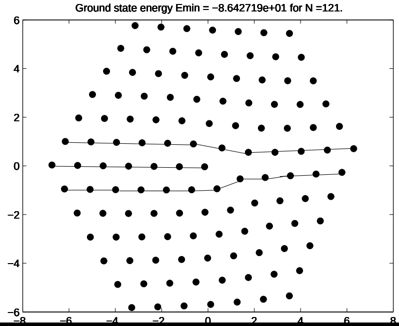


Numerical observations

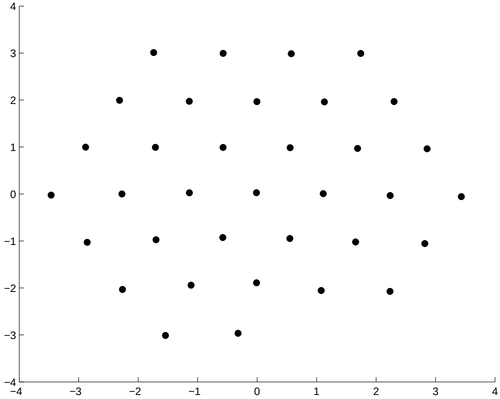
E.g. in Krainyukova (2007)
If $d = 3$ and $V = V_{\mathrm{LJ}}$, then for large n the ground state

$$\{y_i^{\mathrm{min}}\}_{i=1\ldots n} \subset \mathbb{R}^3$$

is approximately a subset of the three-dimensional hcp-lattice up to rotations, translations and dilations.

Boundary layers

It cannot be expected that minimizers are translated, rotated and dilated subset of a lattice.



Surface relaxation

Simplification: Assume that the bulk structure is known and consider an energy

$$E_n(\Omega) = \min\left\{ \sum_{\substack{i,j \in \mathbb{Z}^2 \\ i,j \in n\,\Omega}} \frac{a_{|i-j|}}{2} \left(|y_i - y_j| - b_{|i-j|}\right)^2 \,\middle|\, y \right\}$$

Theorem. (T. '11) If $\lim_{n\to\infty}(b_{\sqrt{2}} - \sqrt{2}b_1) = 0$ and $b_\lambda = 0$ for all $\lambda > \sqrt{2}$, then there exist a constant $E_{\rm bulk}$ and a surface energy density functions $E_{\rm rel}(\nu)$ such that

$$\lim_{n\to\infty} \frac{1}{(b_{\sqrt{2}} - \sqrt{2}b_1)n}\left(E_n(\Omega) - n^2 E_{\rm bulk}\right) = \int_{\partial\Omega} E_{\rm rel}(\nu(x))\, \mathrm{d}H^1(x).$$

$E_{\rm rel}(\nu)$ can be computed by solving an algebraic Riccati-eqn.

Outline

2 Dimensions

Theorem 1. (Ground state energy, T. '06) There exists a constant $\alpha_0 > 0$ such that for all $\alpha \in (0, \alpha_0)$ and for all potentials $V \in C^2((0,\infty))$ with the properties

$$\min_{r>0} \sum_{k \in A_2 \setminus \{0\}} V(rk) = \sum_{k \in A_2 \setminus \{0\}} V(k) = -6,$$

$$V(r) \geq \frac{1}{\alpha} \text{ for } 0 < r < 1-\alpha,$$

$$V''(r) \geq 1 \text{ for } 1-\alpha < r < 1+\alpha,$$

$$|V''(r)| \leq \alpha r^{-7} \text{ for } 1+\alpha < r,$$

the identity

$$\lim_{n\to\infty} \min_{y \in \mathbb{R}^{2\times n}} \frac{1}{n} \sum_{1 \leq i < j \leq n} V(|y_i - y_j|) = -3 \text{ holds.}$$

Ground states

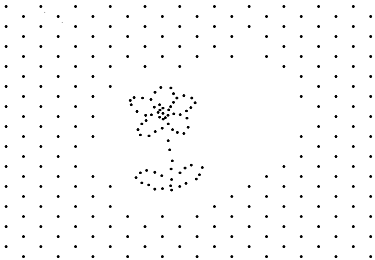
Corollary.

Let $\mathcal{A} \subset A_2$ be finite and assume that $y : A_2 \to \mathbb{R}^2$ is a ground state of

$$\sum_{i \in \mathcal{A},\, j \in \mathcal{L} \setminus \{i\}} V(|y_i - y_j|)$$

subject to the constraint $y_i = i$ for all $i \in A_2 \setminus \mathcal{A}$. Then

$$\{y_i \mid i \in A_2\} = A_2.$$



3 Dimensions

Theorem 2. (Ground state energy, Harris-T. '11)
Let $d = 3$, $\mathcal{L}$ be the fcc lattice and $\rho(r) = \min\left\{1, r^{-10}\right\}$. There exists an open set $\Omega \subset C^2_\rho([0,\infty)) \times C^2([0,\infty) \times [0,\infty))$ such that for all all $V_2, V_3 \in \Omega$ the identity

$$\liminf_{n\to\infty} \min_{y\in\mathbb{R}^{3\times n}} \tfrac{1}{n} E_n(y) = E_*$$
$$= \min_r \left(\frac{1}{2} \sum_{k\in\mathcal{L}\setminus\{0\}} V_2(r\,|k|) + \frac{1}{6} \sum_{k,k'\in\mathcal{L}} V_3(r\,k, r\,k') \right).$$

holds.

Previous mathematical results

$d = 1$: The minimizers are periodic up to a boundary layer.
(Radin ’79, Ping Lin ’01, LeBris-Blanc ’02)

$d = 2$: V is compactly suppported (only nearest-neighbor interactions matter). Gardener, Heitmann, Radin, Schulman, Wagner ’79-’83
T ’06 Long-range potentials.

$d = 3$: V is long-range and very oscillatory, no lattice selected. András Suto, ’05.

Outline

Sketch of the proof

Step 1: Local analysis: Neighborhood graph, defects.

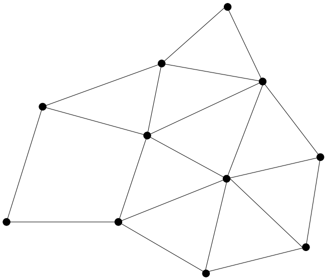
Step 2: Construct local reference configurations

Step 3: Treat non-local terms using cancelations and rigidity estimates

Step 1: Local analysis

- Minimum particle spacing: $|y_i - y_{i'}| > 1 - \alpha$ for all $i \neq i'$ since particles can be moved to infinity.
- Construction of a graph: $\{i, i'\} \in \mathcal{B} \Leftrightarrow |y_i - y_{i'}| \in (1 - \alpha, 1 + \alpha)$
- Musin's (2005) proof of the 3d-kissing problem:

$$\#\{b \in \mathcal{B} \mid i \in b\} \leq 12$$



Local Analysis

Neighborhood:

$$\mathcal{N}(i) = \{i' \mid \{i, i'\} \in \mathcal{B}\}$$

Theorem. (Harris/Tarasov/Taylor/T.)
If $\#\mathcal{N}(i) \geq 12$ and $\#\mathcal{B} \cap \mathcal{N}(i) \geq 24$, then the graph $(\mathcal{N}(i), \mathcal{B} \cap \mathcal{N}(i))$ is either the net of a cubeoctahedron, or a twisted cubeoctahedron.

Earlier (unpublished) results: G. Friesecke.

A conjecture

Let $Z \subset \mathbb{R}^3$ satisfy that $\min_{z' \neq z} |z - z'| \geq 1$ for all $z \in Z$. A point $z \in Z$ is regular if there exists $N(z) \subset Z$ such that $|z - z'| = 1$ for all $z' \in N(z)$ and $\#N(z) \geq 12$.

Conjecture: If z, z' are both regular and $|z - z'| = 1$, then $\#(N(z) \cap N(z')) \geq 4$.

The conjecture above implies that the main theorem holds with $V_3 \equiv 0$.

Sketch of the proof

There are 1,382,779 graphs with 12 vertices, at least 24 edges, at most 5 edges adjacent to any given vertex.
Contact graphs are those graphs where edges are induces by vertex positions.
For each contact graph we define angles $u_j \in [0, 2\pi]$ subtended by edges.
The angles satisfy linear inequalities such as

$$\min_j u_j \geq \arccos(\tfrac{1}{3}),$$

$$\sum_{j \text{ adjacent to vertex } i} u_j = 2\pi,$$

$$\vdots$$

Only for two graphs the corresponding linear programming problems admit a solution.

Defects

$\partial X = \{i \,|(\mathcal{N}(i), \mathcal{B} \cap \mathcal{N}(i))$ is not the graph of a cubeocathedron$\}$.

Cubeoctahedron: 24 edges with length $\sqrt{3}$

Twisted cubeoctahedron: 3 edges with length $\sqrt{8/3}$, 18 edges with length $\sqrt{3}$.
After normalization:

$$V_2\left(\sqrt{8/3}\right) - 3V_2\left(\sqrt{3}\right) \geq \varepsilon.$$

Strategy: Show that

$$E(y) \geq (N - \#\partial X)V^* + \sum_{\{x,x'\}\in B} \frac{1}{C}(|y(x) - y(x')| - 1)^2 + \frac{1}{C}\#\partial X.$$

with $V^* = \min_r \sum_{k\in\mathcal{L}\setminus\{0\}} V(r|k|)$.

Step 2: Construction of local reference configurations

Theorem. For all domains $\Omega' \subset \Omega \subset \mathbb{R}^2$ with the properties $\mathrm{dist}(\Omega', \partial\Omega) \geq 3\mathrm{diam}(\Omega') + 2$, Ω is convex and $\Omega \cap y(\partial X) = \emptyset$ there exists a discrete orientation preserving imbedding $\Phi : \omega \to \mathcal{L}$, where $\omega = y^{-1}(\Omega')$.

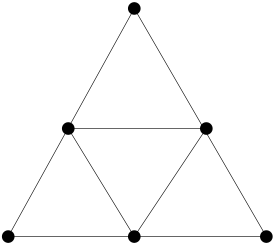
Step 3: Nonlocal terms

Two different ideas are needed.

A) Discrete rigidity estimates

B) Cancelation of the ghost forces

Use geometric rigidity of the system in order to control errors:



If the small triangles are undistorted, then the big triangle is undistorted.

Continuum rigidity results

$u \in C^1(\Omega, \mathrm{R}^d)$, $\Omega \subset \mathrm{R}^d$.

- $\nabla u \in SO(d) \Rightarrow \nabla u = \mathrm{const}$ (Liouville).
  More general treatment: Gromov's book "Partial differential relations" (1986).
- $|(\nabla u)^T \nabla u - \mathrm{Id}| \ll 1 \Rightarrow Du$ is almost constant (Reshetnyak, 1967).
- $\int |\nabla u - R|^2 \,\mathrm{d}x \leq C \int |\nabla u - SO(d)|^2 \,\mathrm{d}x$
  (Friesecke, James & Müller, CPAM 2002).

Estimates for rotations

We need an estimate on the difference between average local rotations and the global rotation

$$\left| R - \frac{1}{|\Omega|} \int_{\Omega} R(x)\,\mathrm{d}x \right| \leq C \int |\nabla u - SO(3)|^2\,\mathrm{d}x,$$

where R minimizes $\int_{\Omega} |R - \nabla u(x)|^2\,\mathrm{d}x$.

Summary

- Sharp lower bound for the interaction energy

$$V^* \le \frac{1}{n} \min_{y \in \mathbb{R}^{3\times n}} E(y) \le V^* + O\left(n^{-\frac{1}{3}}\right).$$

- $$V^* = \min_r \left(\frac{1}{2} \sum_{k \in \mathcal{L}\setminus\{0\}} V_2(r|k|) + \frac{1}{6} \sum_{k,k' \in \mathcal{L}\setminus\{0\}} V_3(rk, rk') \right)$$

  is the binding energy per particle
- Minimizers are periodic and form an fcc-lattice if periodic or Dirichlet-boundary conditions are applied.
- Open problems
  - Fourier-based methods
  - Local minimizers such as dislocations
  - Finite temperature, gradient fields

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