Crystal problems for binary systems

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Introduction: ionic solids

Salt NaCl

Combination of bonding, size of ions, orbitals... ⇒ Structure
Introduction: ionic solids

- Mathematical justification of these structures: very difficult problem.
- Identical particles / optimization of structure: several open problems.
- Two approaches (in this talk) via energy optimization:
  1. fixing the lattice structure and optimizing the charge distribution;
  2. fixing the charge distribution and optimizing the structure ($d = 1$).

In both cases: the interaction is electrostatic (and more general).
Born’s problem for the electrostatic energy (1921)

Max Born (1882-1970)

“How to arrange positive and negative charges on a simple cubic lattice of finite extent so that the electrostatic energy is minimal?”

Über elektrostatische Gitterpotentiale, Zeitschrift für Physik, 7:124-140, 1921
Conjecture [Born ’21]
The alternate configuration of charges is the unique solution among all periodic distributions of charges on $\mathbb{Z}^3$.

The total amount of charge is fixed and the neutrality have to be assumed.
Born’s result in dimension 1 (1921)

Born proved the conjecture in dimension 1 (Ewald summation method).

Assuming that $\varphi_0 > 0$, $\sum_{i=1}^{N} \varphi_i^2 = N$ and $\sum_{i=1}^{N} \varphi_i = 0$, he proved the optimality of the alternate configuration $\varphi_i = (-1)^i$, achieved for $N \in 2\mathbb{N}$. 
Crystallization in dimension 1

Identical particles and symmetric potential:

1. **Ventevogel ’78**: convex functions, Lennard-Jones-type potentials.

2. **Ventevogel-Nijboer ’79**: Gaussian, more general repulsive-attractive potentials, positivity of the Fourier transform.

3. **Gardner-Radin ’79**: classical (12, 6) Lennard-Jones by alternatively adding points from both sides of the configuration.
Crystallization for one-dimensional alternate systems

We consider periodic configurations of alternate kind of particles. \( \rho \): length. \( N \): number of point per period (\( N = 8 \) in the example).

They interact by three kind of potentials: \( f_{12} \), \( f_{11} \) and \( f_{22} \).

**Theorem [B.-Knüpfer-Nolte ’18] (soon on arXiv)**

If \( f_{12}(x) = -f_{11}(x) = -f_{22}(x) = -x^{-p}, \ p \geq 0.66 \), then, for any \( \rho > 0 \) and any \( N \geq 1 \), the **equidistant** configuration is the **unique maximizer** of the total energy per point among all the periodic configurations of points.

Proof based on Jensen’s inequality.

The same occurs for many systems (at high density).
Back to Born’s conjecture: charge and potential

- **Bravais lattice** $X = \bigoplus_{i=1}^{d} \mathbb{Z} u_i$ of **covolume 1**, i.e. $|Q| = 1$ (unit cell).

- **Distribution of charge** $\varphi : X \to \mathbb{R}$, s.t. $x \in X$ has charge $\varphi_x = \varphi(x)$.

**$N$-periodicity**: $\varphi \in \Lambda_N(X)$, i.e. $\forall x \in X, \forall i, \varphi(x + Nu_i) = \varphi(x)$.

**The total charge is fixed**:\n\[ \sum_{y \in K_N} \varphi_y^2 = N^d. \] We assume $\varphi_0 > 0$.

**Periodicity cube** $K_N := \left\{ x = \sum_{i=1}^{d} m_i u_i \in X ; 0 \leq m_i \leq N - 1 \right\}$.

We note $K_N^*$ the same cube for the **dual lattice** $X^*$.

- **Potential** $f(x) = \int_0^\infty e^{-|x|^2 t} d\mu_f(t)$, Borel measure $\mu_f \geq 0$,
\[ i.e. \quad f(x) = F(|x|^2) \] where $F$ is completely monotone.
Energy minimization problem

Definition of the energy

\[ \mathcal{E}_{X,f}[\varphi] := \lim_{\eta \to 0} \left( \frac{1}{2N^d} \sum_{y \in K_N} \sum_{x \in X \setminus \{0\}} \varphi_y \varphi_{x+y} f(x) e^{-\eta|x|^2} \right), \]

where we assume \( \sum_{y \in K_N} \varphi_y = 0 \) if \( f \not\in \ell^1(X \setminus \{0\}) \) (charge neutrality).

Problem: Minimizing \( \mathcal{E}_{X,f} \) among all \( N \) and all \( \varphi \in \Lambda_N(X) \) satisfying

\[ \sum_{y \in K_N} \varphi_y^2 = N^d \quad \text{and} \quad \varphi_0 > 0. \]

[B.-Knüpfer ’17]

1. General strategy connecting \( \mathcal{E}_{X,f} \) with lattice theta function.
2. Explicit solution for \( X \) orthorhombic or triangular (uniqueness).
The space $\Lambda_N(X)$ of $N$-periodic charges

$\Lambda_N(X)$ is equipped with inner product and norm:

$$ (\varphi, \psi)_{K_N} = \sum_{y \in K_N} \varphi(y) \overline{\psi(y)}, \quad \|\varphi\| = \sqrt{(\varphi, \varphi)_{K_N}}. $$

**Discrete Fourier transform:** $\varphi \in \Lambda_N(X) \Rightarrow \hat{\varphi} \in \Lambda_N(X^*)$ s.t. $\forall k \in X^*$,

$$ \hat{\varphi}(k) = \frac{1}{N^{d/2}} \sum_{y \in K_N} \varphi_y e^{-\frac{2\pi i}{N} y \cdot k}. $$

Discrete inverse Fourier transform of $\psi \in \Lambda_N(X^*)$: for any $x \in X$,

$$ \check{\psi}(x) = \frac{1}{N^{d/2}} \sum_{y \in K_N^*} \psi_y e^{\frac{2\pi i}{N} y \cdot x}. $$
The autocorrelation function $s = \varphi \ast \varphi$

Let $\varphi : X \to \mathbb{R}$ be $N$-periodic such that $\sum_{y \in K_N} \varphi_y^2 = N^d$, then we define

$$s_x = \sum_{y \in K_N} \varphi_y \varphi_{y+x}.$$

**Properties of $s$**

- $s \in \Lambda_N(X)$,
- $s_{-x} = s_x$,
- $\sum_{x \in K_N} s_x = \left( \sum_{x \in K_N} \varphi_x \right)^2$,
- $s_0 = N^d$. 
The inverse Fourier transform $\xi$

We define $\xi := N^{-\frac{d}{2}} \hat{s}$, i.e. for any $k \in X^*$ and any $x \in X$,

$$\xi_k := \frac{1}{N^d} \sum_{y \in K_N} s_y e^{\frac{2\pi i}{N} y \cdot k}, \quad s_x = \sum_{k \in K_N^*} \xi_k e^{-\frac{2\pi i}{N} k \cdot x}.$$ 

Properties of $\xi$

- $\xi_k \in \mathbb{R}$,
- $\xi_{-k} = \xi_k$,
- $\xi_k = |\check{\varphi}_k|^2 \geq 0$,
- $\xi_0 = \frac{1}{N^d} \left( \sum_{x \in K_N} \varphi_x \right)^2$,
- $\sum_{k \in K_N^*} \xi_k = N^d$. 

Laurent Bétermin (KU)
Absolutely summable case

We assume that $f \in \ell^1(X\backslash\{0\})$, then

$$E_{X,f}[\varphi] = \lim_{\eta \to 0} \left( \frac{1}{2N^d} \sum_{y \in K_N} \sum_{x \in X\backslash\{0\}} \varphi_y \varphi_{x+y} f(x) e^{-\eta|x|^2} \right)$$

$$= \frac{1}{2N^d} \sum_{y \in K_N} \sum_{x \in X\backslash\{0\}} \varphi_y \varphi_{x+y} f(x)$$

$$= \frac{1}{2N^d} \sum_{x \in X\backslash\{0\}} s_x f(x)$$

$$= \frac{1}{2N^d} \sum_{k \in K_N^*} \xi_k \sum_{x \in X\backslash\{0\}} e^{\frac{2\pi i}{N} x \cdot k} f(x)$$

$$= \frac{1}{2N^d} \sum_{k \in K_N^*} \xi_k E[k].$$
Rewriting $E$ in terms of translated theta function

Since $f(x) = \int_0^\infty e^{-|x|^2 t} d\mu_f(t)$, we obtain, $\forall k \in K_\mathbb{N}^*$,

$$E[k] = \sum_{x \in X \setminus \{0\}} e^{\frac{2\pi i}{N} x \cdot k} f(x)$$

$$\quad = \int_0^\infty \left( \sum_{x \in X} e^{-|x|^2 t} e^{\frac{2\pi i}{N} x \cdot k} - 1 \right) d\mu_f(t)$$

$$\quad = \int_0^\infty \left( \pi^\frac{d}{2} t^{-\frac{d}{2}} \sum_{p \in X^*} e^{-\frac{\pi^2}{t} |p + \frac{k}{N}|^2} - 1 \right) d\mu_f(t)$$

$$\quad = \int_0^\infty \left( \pi^\frac{d}{2} t^{-\frac{d}{2}} \theta_{X^* + \frac{k}{N}} \left( \frac{\pi}{t} \right) - 1 \right) d\mu_f(t).$$

$z_0$ minimizer of $z \mapsto \theta_{X^* + z}(\alpha)$ for all $\alpha > 0 \Rightarrow k_0 = Nz_0$ minimizer of $E$. 
From $\xi$ to $\varphi$: existence of a minimizer for $E_{X,f}$

**Lemma**

If $\xi \in \Lambda_N(X^*)$, $\xi \geq 0$, $\xi_{-k} = \xi_k$ and $\sum_{k \in K^*_N} \xi_k = N^d$, then $\varphi$ defined by

$$\varphi_x = \frac{1}{N^\frac{d}{2}} \sum_{k \in K^*_N} \sqrt{\xi_k} \cos \left( \frac{2\pi}{N} x \cdot k \right)$$

satisfies $\sum_{y \in K_N} \varphi_y^2 = N^d$, $s_x = \sum_{y \in K_N} \varphi_y \varphi_{y+x}$, $\xi = N^{-\frac{d}{2}} \xi$.

If $k_0 = Nz_0$ minimizes $E$, we have that $\xi$, defined by $\xi_{k_0} = N^d$ and $\xi_k = 0$ otherwise, is a minimizer of $\xi \mapsto E_{X,f}[\varphi]$, which corresponds to

$$\varphi_x = c \cos(2\pi x \cdot z_0), \quad x \in X, \quad c \text{ constant}.$$
From $\xi$ to $\varphi$: uniqueness of the minimizer for $E_{X,f}$

We assume that $k \mapsto \theta_{X^*} + \frac{k}{N}(\alpha)$ has at most two minimizers $k_0$ and $k_1$ in $X^*$ for some $N \in \mathbb{N}$, then:

- $k_0$ and $k_1$ are symmetry related: $\frac{k_1}{N} = \sum_{i=1}^{d} u_i^* - \frac{k_0}{N}$,
- by periodicity and parity of $\xi$, the minimizer of $\xi \mapsto E_{X,f}[\varphi]$ is given by

$$
\xi_{k_0} = \xi_{k_1} = \frac{N^d}{2}, \quad \forall k \in K_N^* \setminus \{k_0, k_1\}, \xi_k = 0.
$$

- Then, we obtain $s_X = N^d \cos\left(\frac{2\pi}{N} k_0 \cdot x\right)$.

Using the fact that $\xi_k = |\tilde{\varphi}|^2$, we reconstruct the unique solution $\varphi$ such that $\varphi_0 > 0$:

$$
\varphi_x = c \cos(2\pi x \cdot z_0), \quad x \in X, \quad c \text{ constant}.
$$

$\Rightarrow$ Any minimizer is neutral: $\sum_{y \in K_N} \varphi_y = 0$ (general fact).
Translated lattice theta function

For a Bravais lattice $X \subset \mathbb{R}^d$ and a point $z \in \mathbb{R}^d$ and $\alpha > 0$, we define

$$
\theta_{X+z}(\alpha) := \sum_{x \in X} e^{-\pi \alpha |x+z|^2}.
$$

We have $\theta_{X+z}(\alpha) = \frac{1}{\alpha^d} P_X (z, \frac{1}{4\pi \alpha})$ where $P_X$ solves the heat equation

$$
\begin{cases}
\partial_t P_X(z, t) = \Delta_z P_X & \text{for } (z, t) \in \mathbb{R}^d \times (0, \infty) \\
P_X(z, 0) = \sum_{p \in X} \delta_p & \text{for } z \in \mathbb{R}^d.
\end{cases}
$$
Minimization of $z \mapsto \theta_{X+z}(\alpha)$ for fixed $X$ and $\alpha$

**Proposition [B.-Petrache ’17]: The orthorhombic case**

Let $d \geq 1$ and $X = \bigoplus_{i=1}^{d} \mathbb{Z}(a_i e_i)$ of unit cell $Q$, where $a_i > 0$ for any $1 \leq i \leq d$. Then, for any $\alpha > 0$, the center of the unit cell $z^* = \frac{1}{2}(a_1, \ldots, a_d)$ is the unique minimizer in $Q$ of $z \mapsto \theta_{X+z}(\alpha)$.

**Proof:** Based on Montgomery argument for $1d$ theta function (Jacobi triple product) and the fact that $\theta_{X+z}(\alpha)$ is a product of $1d$ theta functions.

**Proposition [Baernstein II ’97]: the triangular lattice case**

Let $\alpha > 0$ and $A_2 = \mathbb{Z}(1, 0) \oplus \mathbb{Z}(1/2, \sqrt{3}/2)$ of unit cell $Q$, then the minima of $z \mapsto \theta_{A_2+z}(\alpha)$ in $Q$ are the two barycenters of the primitive triangles $z_1^* = (1/2, 1/(2\sqrt{3}))$ and $z_2^* = (1, 1/\sqrt{3})$.

**Proof:** Use of the heat equation and symmetries of $A_2$. 
Minimization of $z \mapsto \theta_{X+z}(\alpha)$ for fixed $X$ and $\alpha$
Orthorhombic case

- If $X = \bigoplus_{i=1}^{d} \mathbb{Z}(a_i e_i)$, $a_i > 0$, then $X^* = \bigoplus_{i=1}^{d} \mathbb{Z} u_i^*$, $u_i^* = a_i^{-1} e_i$.

- $k \mapsto E[k]$ is minimized by (only achieved if $N \in 2\mathbb{N}$)

  $$k_0 = Nz_0 = \frac{N}{2} (u_1^*, ..., u_d^*).$$

- $\xi \mapsto \mathcal{E} \chi, f[\varphi]$ is minimized by

  $$\xi_{k_0} = N^d, \quad \forall k \neq k_0, \xi_k = 0.$$

- The minimizing configuration is, for $x = \sum_{i=1}^{d} n_i u_i$, $n_i \in \mathbb{Z}$,

  $$\varphi^*_x = \cos (2\pi x \cdot z_0) = \cos \left( \pi x \cdot \sum_{i=1}^{d} u_i^* \right) = (-1)^\sum_{i=1}^{d} n_i.$$
The orthorhombic case: optimal distribution of charges


The triangular lattice case: honeycomb configuration

\[ \Lambda_1 = \sqrt{\frac{2}{3}} \left[ \mathbb{Z}(1, 0) \oplus \mathbb{Z}\left(\frac{1}{2}, \sqrt{3}/2\right) \right] \Rightarrow \Lambda_1^* = \sqrt{\frac{2}{3}} \left[ \mathbb{Z}\left(\sqrt{3}/2, -1/2\right) \oplus \mathbb{Z}(0, 1) \right] \]

- The minimizers of \( k \mapsto E[k] \) are

\[ k_0 = \frac{N}{3}(u_1^* + u_2^*), \quad \text{and} \quad k_1 = \frac{2N}{3}(u_1^* + u_2^*). \]

- The minimizing configuration, only achieved if \( N \in 3\mathbb{N} \), is

\[ \varphi^*(mu_1 + nu_2) = \sqrt{2} \cos \left( \frac{2\pi}{3}(m + n) \right). \]
Charge: $-\frac{\sqrt{2}}{2}$. Charge: $+\sqrt{2}$. 
Honeycomb configuration: Sodium Sulfide


T = 500K

Sodium Sulfide

(Na$_2$S)

Na$^+$

(3S$^{2-}$ neighbors)

S$^{2-}$

(6Na$^+$ neighbors)

60 Na$^+$ ions

30 S$^{2-}$ ions

10 Å
The nonsummable case: Ewald summation

We assume \( \sum_{y \in K_N} \varphi_y = 0 \) and we recall that 
\[
f(x) = \int_0^\infty e^{-t|x|^2} \, d\mu_f(t).
\]

We write 
\[
f(x)e^{-\eta|x|^2} = \int_0^{\nu^2} e^{-(t+\eta)|x|^2} \, d\mu_f(t) + \int_{\nu^2}^\infty e^{-(t+\eta)|x|^2} \, d\mu_f(t).
\]

Let 
\[
f^{(1)}(x) = \int_{\nu^2}^\infty e^{-t|x|^2} \, d\mu_f(t) \quad \text{and} \quad f^{(2)}(x) = \pi^\frac{d}{2} \int_0^{\nu^2} t^{\frac{d}{2}} e^{-\frac{\pi^2}{t} |x|^2} \, d\mu_f(t)
\]

\[
\mathcal{E}_{X,f}[\varphi] = \lim_{\eta \to 0} \left( \frac{1}{2N^d} \sum_{x \in X \setminus \{0\}} s_x f(x)e^{-\eta|x|^2} \right)
\]
\[
= \left( \sum_{k \in \mathbb{Z}^N} \xi_k \left( \sum_{x \in X \setminus \{0\}} e^{\frac{2i\pi}{N} x \cdot k} f^{(1)}(x) + \sum_{q \in X^*} f^{(2)} \left( q + \frac{k}{N} \right) \right) \right) - \frac{\mu_f([0,\nu^2])}{2}
\]
Let $f_1^{(\nu)}(x) = \int_{\nu^2}^{\infty} e^{-t|x|^2} d\mu_f(t)$ and $f_2^{(\nu)}(x) = \pi^{\frac{d}{2}} \int_0^{\nu^2} t^{-\frac{d}{2}} e^{-\frac{\pi^2 t}{t} |x|^2} d\mu_f(t)$

We then have to minimize

$F[k] := \sum_{x \in X \setminus \{0\}} e^{\frac{2\pi i}{N} x \cdot k} f_1^{(\nu)}(x) + \sum_{q \in X^*} f_2^{(\nu)}(q + \frac{k}{N})$

$$= \int_{\nu^2}^{+\infty} \sum_{x \in X \setminus \{0\}} e^{\frac{2\pi i}{N} x \cdot k} e^{-t|x|^2} d\mu_f(t) + \pi^{\frac{d}{2}} \int_0^{\nu^2} \left( \sum_{q \in X^*} e^{-\frac{\pi^2 t}{t} |q + \frac{k}{N}|^2} \right) t^{-\frac{d}{2}} d\mu_f(t)$$

$$= \int_{\nu^2}^{\infty} \left( \frac{\pi^{\frac{d}{2}}}{t^{\frac{d}{2}}} \theta_{X^* + \frac{k}{N}} \left( \frac{\pi}{t} \right) - 1 \right) d\mu_f(t) + \pi^{\frac{d}{2}} \int_0^{\nu^2} \theta_{X^* + \frac{k}{N}} \left( \frac{\pi}{t} \right) t^{-\frac{d}{2}} d\mu_f(t).$$

We conclude as in the absolutely summable case.
In [B.-Knüpfer '17], we proved:

- **Absolute summable** \( f \): any minimizer of \( E_{X,f} \) among \( \varphi \in \Lambda_N(X) \) such that \( \sum_{y \in K_N} \varphi_y^2 = N^d \) is neutral, i.e. \( \sum_{y \in K_N} \varphi_y = 0 \).

- If we know the (at most two) minimizer \( z_0 \in \frac{1}{N} X^* \) of \( z \mapsto \theta_{X^* + z}(\alpha) \) for any \( \alpha > 0 \), the **unique** minimizing \( N \)-periodic configuration \( \varphi^* \) such that \( \varphi_0^* > 0 \) and \( \sum_{y \in K_N} (\varphi_y^*)^2 = N^d \) is given, for any \( x \in X \), by

  \[ \varphi_x^* = c \cos(2\pi x \cdot z_0). \]

- For orthorhombic lattices, \( \varphi^* \) is the **alternation of charges** \(-1\) and \(1\).

- For the triangular lattice, \( \varphi^* \) is a **honeycomb configuration**.
Open problems

- $d = 2$: $X$ rhombic or asymmetric.

- $d = 2$: $f(x) = - \log |x| = \frac{1}{2} \lim_{\varepsilon \to 0} \left( \int_{\varepsilon}^{\infty} \frac{e^{-t|x|^2}}{t} dt + \gamma + \log \varepsilon \right)$

- $d = 3$: $X \in \{FCC, BCC\}$.

- Smeared out particles (radially symmetric or orbitals).

- Replace $f$ by $\tilde{f}(x - y) = \frac{1}{|x - y|^2} + \frac{\varphi_x \varphi_y}{|x - y|}$ (Pauli exclusion principle).

- Find a lattice $X$ without a periodic optimal configuration of charges $\varphi^* : X \to \mathbb{R}$.

- Study the $\alpha$-dependence of $\min_{z \in Q} \theta_{X+z}(\alpha)$. 
Escher - Cubic space division, 1953.

Thank you for your attention!