Crystal problems for binary systems

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Talk based on joint works with **H. Knüpfer**, **F. Nolte** and **M. Petrache**

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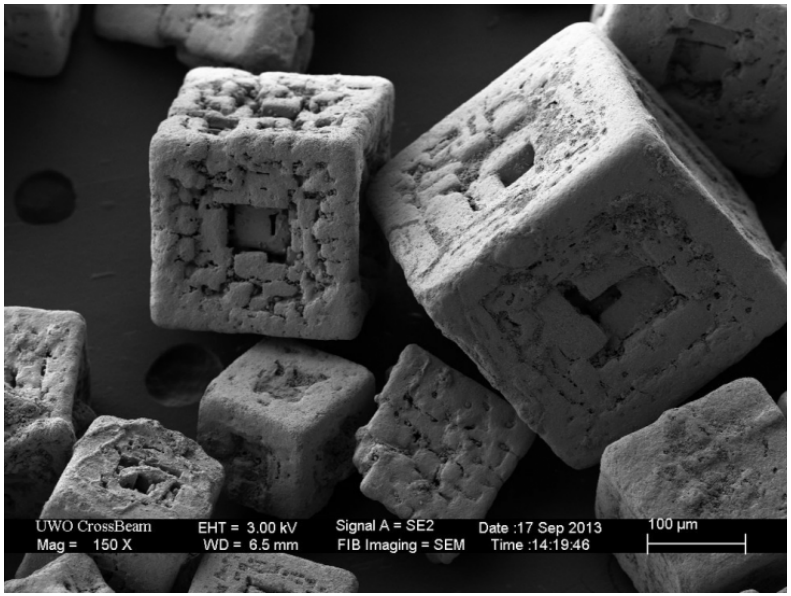
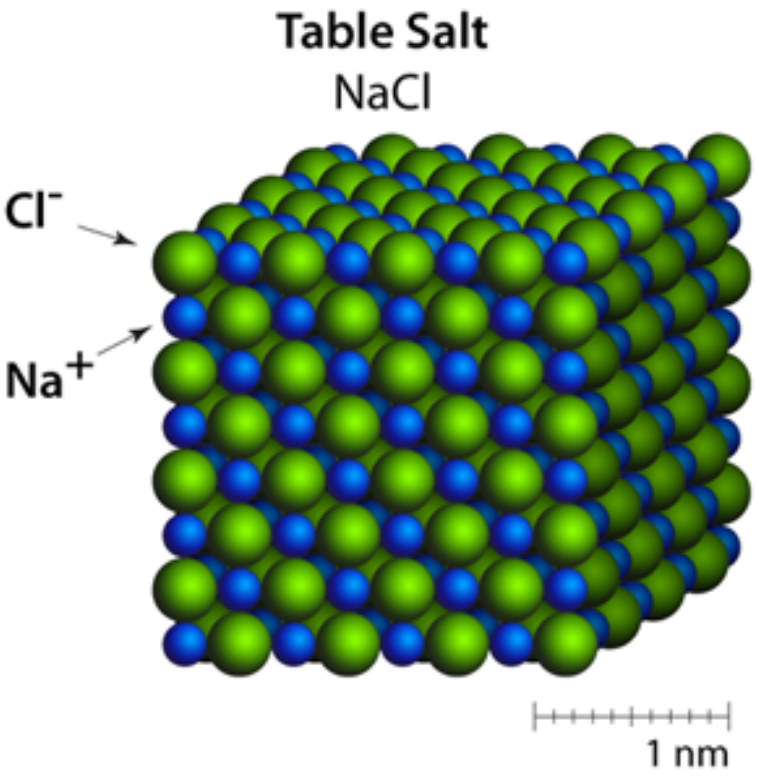
Introduction: ionic solids





Salt NaCl

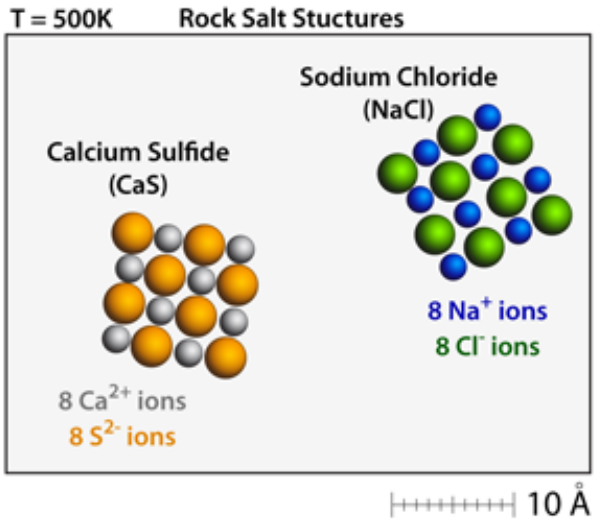
Combination of bonding, size of ions, orbitals... $\Rightarrow$ Structure

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)

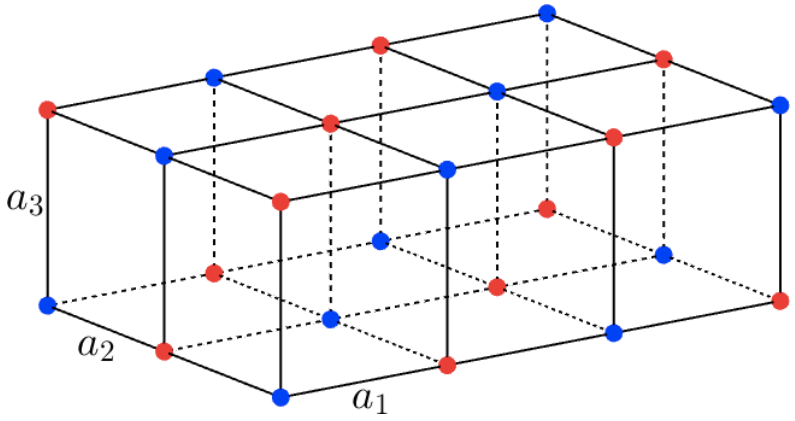
"How to arrange positive and negative charges on a simple cubic lattice of finite extent so that the electrostatic energy is minimal?"

Über elektrostatische Gitterpotentiale,
Zeitschrift für Physik, 7:124-140, 1921

Born's Conjecture (1921)

Conjecture [Born '21]

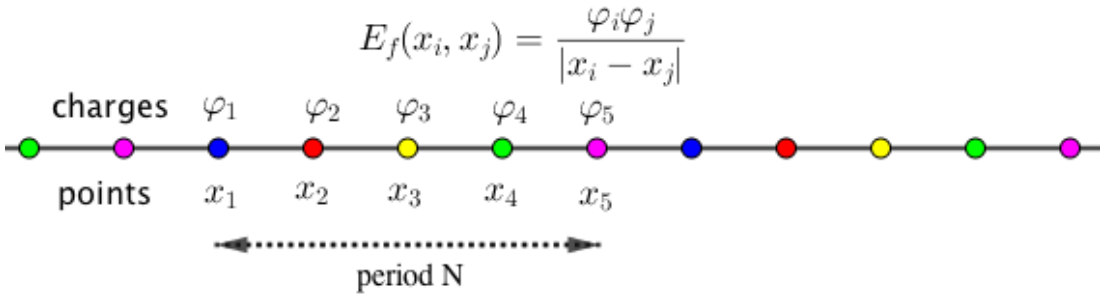
The alternate configuration of charges is the unique solution among all periodic distributions of charges on $\mathbb{Z}^3$.



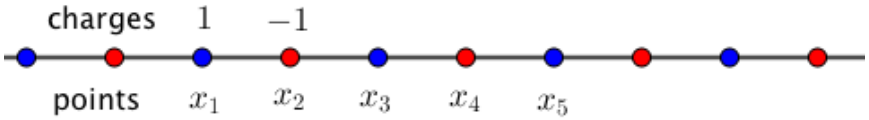
The total amount of charge is fixed and the neutrality have to be assumed.

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 $N \in 2\mathbb{N}$.



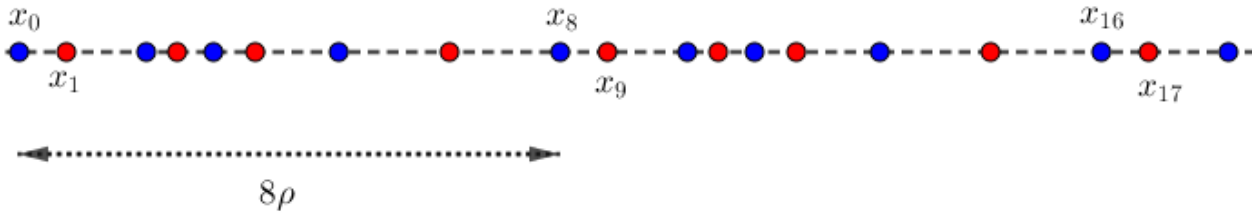
Crystallization in dimension 1

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.
ρ: 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: $\sum_{y \in K_N} \varphi_y^2 = N^d$. 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. $f(x) = F(|x|^2)$ 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 $f\notin \ell^1(X\setminus\{0\})$ (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. $\forall k \in X^*$,

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

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

$$\check{\psi}(x) = \frac{1}{N^{\frac{d}{2}}} \sum_{y \in K_N^*} \psi_y e^{\frac{2\pi i}{N} y \cdot x}.$$

The autocorrelation function $s = \varphi * \varphi$

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 ξ

We define $\xi := N^{-\frac{d}{2}}\check{s}$, 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 ξ

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

Absolutely summable case

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

$$\begin{aligned}
\mathcal{E}_{X,f}[\varphi] &= \lim_{\eta\to 0}\left(\frac{1}{2N^d}\sum_{y\in K_N}\sum_{x\in X\backslash\{0\}}\varphi_y\varphi_{x+y}f(x)e^{-\eta|x|^2}\right)\\
&= \frac{1}{2N^d}\sum_{y\in K_N}\sum_{x\in X\backslash\{0\}}\varphi_y\varphi_{x+y}f(x)\\
&= \frac{1}{2N^d}\sum_{x\in X\backslash\{0\}}s_x f(x)\\
&= \frac{1}{2N^d}\sum_{k\in K_N^*}\xi_k\sum_{x\in X\backslash\{0\}}e^{\frac{2\pi i}{N}x\cdot k}f(x)\\
&= \frac{1}{2N^d}\sum_{k\in K_N^*}\xi_k E[k].
\end{aligned}$$

Rewriting E in terms of translated theta function

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

$$\begin{aligned} E[k] &= \sum_{x \in X \setminus \{0\}} e^{\frac{2\pi i}{N} x \cdot k} f(x) \\ &= \int_0^\infty \left(\sum_{x \in X} e^{-|x|^2 t} e^{2\pi i x \cdot \frac{k}{N}} - 1 \right) d\mu_f(t) \\ &= \int_0^\infty \left(\pi^{\frac{d}{2}} t^{-\frac{d}{2}} \sum_{p \in X^*} e^{-\frac{\pi^2}{t} \left| p + \frac{k}{N} \right|^2} - 1 \right) d\mu_f(t) \\ &= \int_0^\infty \left(\pi^{\frac{d}{2}} t^{-\frac{d}{2}} \theta_{X^* + \frac{k}{N}} \left(\frac{\pi}{t} \right) - 1 \right) d\mu_f(t). \end{aligned}$$

z_0 minimizer of $z \mapsto \theta_{X^*+z}(\alpha)$ for all $\alpha > 0 \Rightarrow k_0 = N z_0$ minimizer of E.

From ξ to φ: existence of a minimizer for $\mathcal{E}_{X,f}$

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

If $k_0 = N z_0$ minimizes E, we have that ξ, defined by $\xi_{k_0} = N^d$ and $\xi_k = 0$ otherwise, is a minimizer of $\xi \mapsto \mathcal{E}_{X,f}[\varphi]$, which corresponds to

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

From ξ to φ: uniqueness of the minimizer for $\mathcal{E}_{X,f}$

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 ξ, the minimizer of $\xi \mapsto \mathcal{E}_{X,f}[\varphi]$ is given by

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

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

Using the fact that $\xi_k = |\check{\varphi}|^2$, we reconstruct the **unique** solution φ 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**: $\displaystyle\sum_{y \in K_N} \varphi_y = 0$ (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 $\theta_{X+z}(\alpha) = \frac{1}{\alpha^{\frac{d}{2}}} P_X\left(z, \frac{1}{4\pi\alpha}\right)$ 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 α

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 $z^* = \frac{1}{2}(a_1, ..., a_d)$ is the unique minimizer in Q of $z \mapsto \theta_{X+z}(\alpha)$.

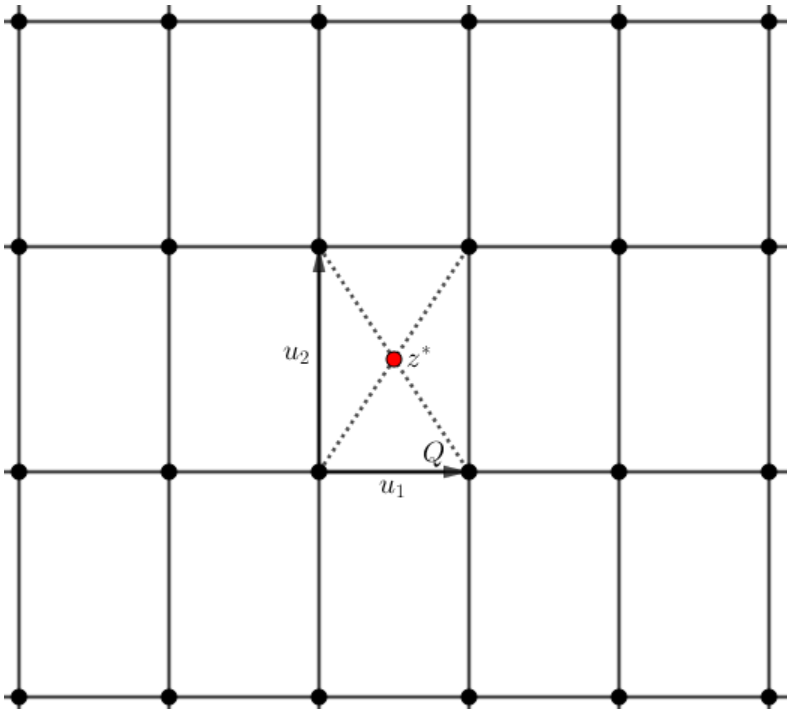
Proof: Based on Montgomery argument for $1d$ theta function (Jacobi triple product) and the fact that $\theta_{X+z}(\alpha)$ is a product of $1d$ theta functions.

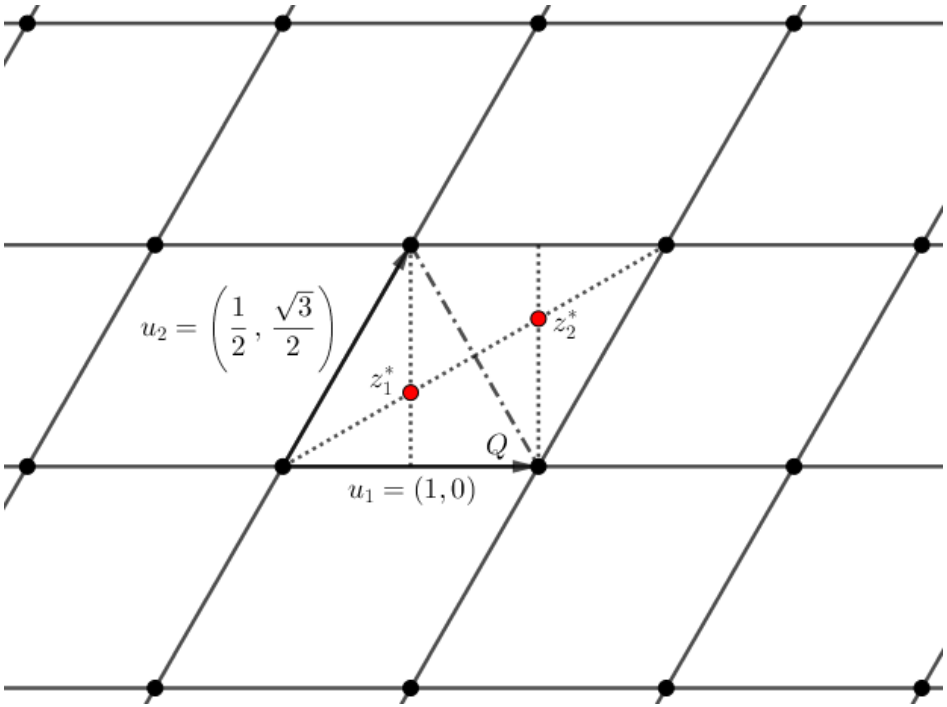
Proposition [Baernstein II '97]: the triangular lattice case

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 α





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 $N \in 2\mathbb{N}$)

$$k_0 = N z_0 = \frac{N}{2} \left(u_1^*, ..., u_d^* \right).$$

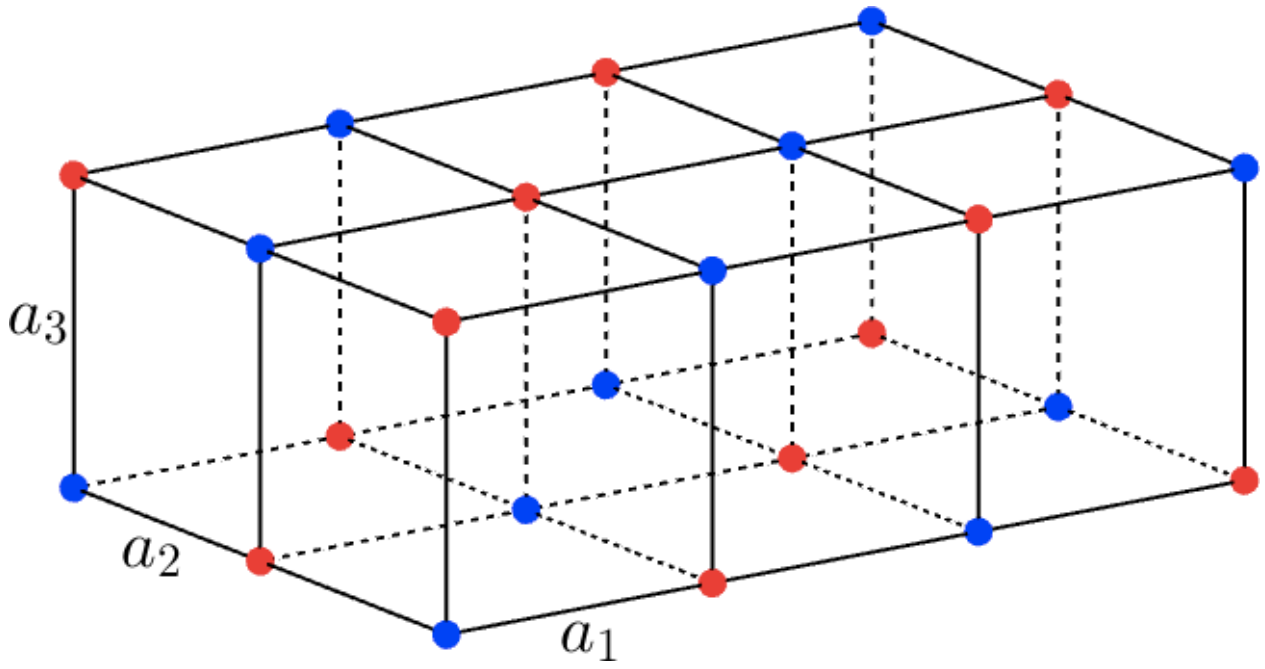
- $\xi \mapsto \mathcal{E}_{X,f}[\varphi]$ is minimized by

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

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

$$\varphi_x^* = \cos\left(2\pi x \cdot z_0\right) = \cos\left(\pi x \cdot \sum_{i=1}^{d} u_i^*\right) = (-1)^{\sum_{i=1}^{d} n_i}.$$

The orthorhombic case: optimal distribution of charges



Charge: -1. Charge: $+1$.

The triangular lattice case: honeycomb configuration

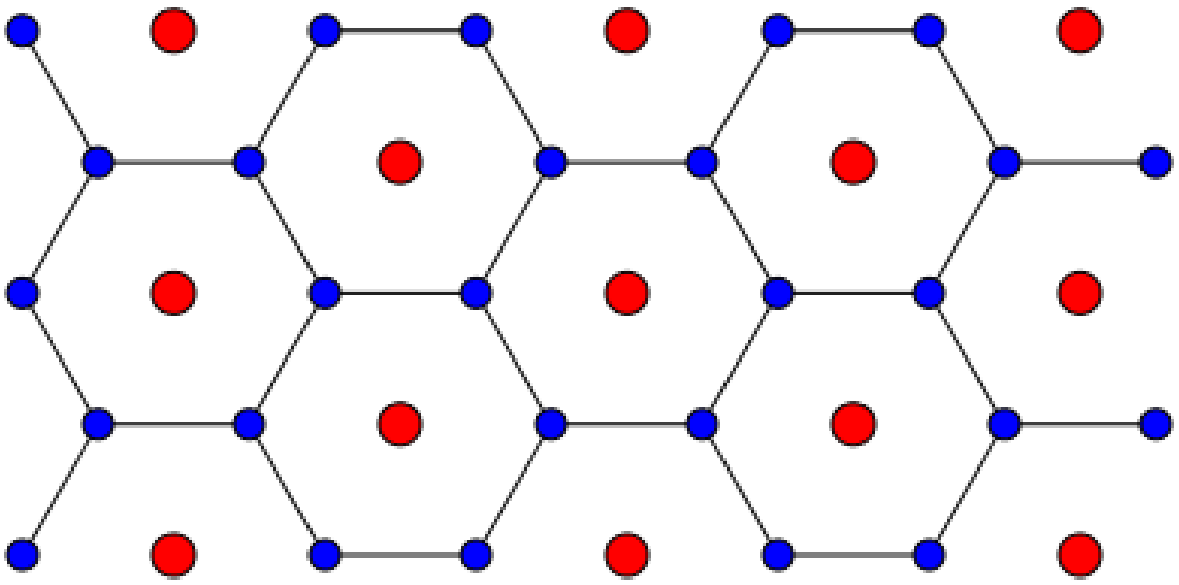
$$\Lambda_1 = \sqrt{\tfrac{2}{\sqrt{3}}}\left[\mathbb{Z}(1,0) \oplus \mathbb{Z}\left(\tfrac{1}{2}, \tfrac{\sqrt{3}}{2}\right)\right] \Rightarrow \Lambda_1^* = \sqrt{\tfrac{2}{\sqrt{3}}}\left[\mathbb{Z}\left(\tfrac{\sqrt{3}}{2}, -\tfrac{1}{2}\right) \oplus \mathbb{Z}(0,1)\right]$$

- The minimizers of $k \mapsto E[k]$ are

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

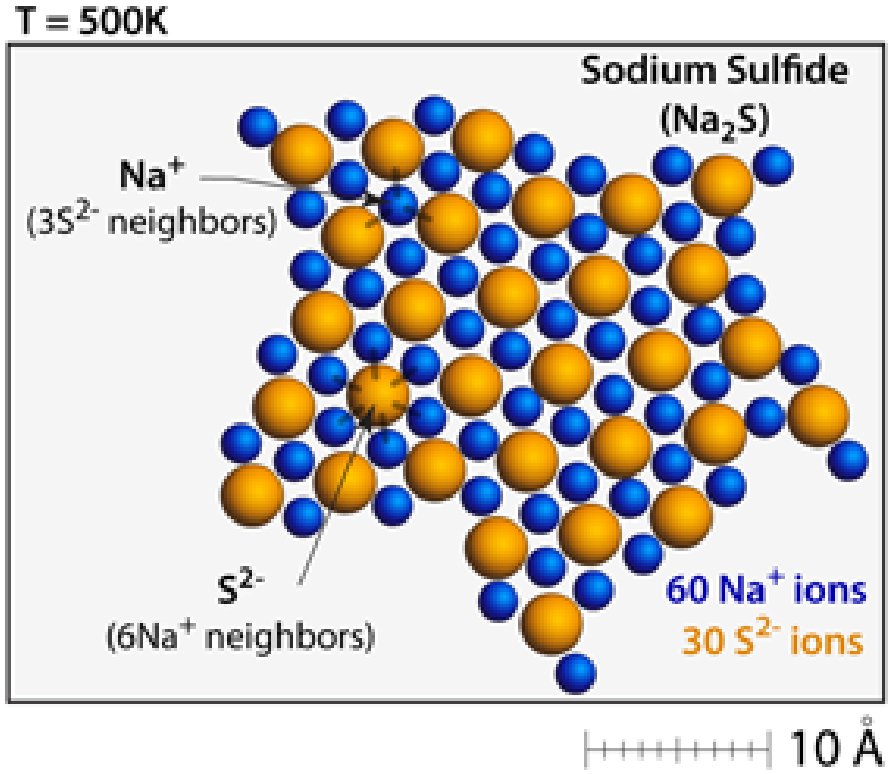
- The minimizing configuration, only achieved if $N \in 3\mathbb{N}$, is

$$\varphi^*(mu_1 + nu_2) = \sqrt{2}\cos\left(\frac{2\pi}{3}(m+n)\right).$$



Charge: $-\frac{\sqrt{2}}{2}$. Charge: $+\sqrt{2}$.

Honeycomb configuration: Sodium Sulfide



Charge: -2. Charge: $+1$.

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 $f_1^{(\nu)}(x) = \int_{\nu^2}^\infty e^{-t|x|^2} d\mu_f(t)$ and $f_2^{(\nu)}(x) = \pi^{\frac{d}{2}} \int_0^{\nu^2} t^{-\frac{d}{2}} e^{-\frac{\pi^2}{t}|x|^2} d\mu_f(t)$

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

$$= \frac{1}{2N^d}\sum_{k\in K_N^*}\xi_k\left(\sum_{x\in X\setminus\{0\}} e^{\frac{2i\pi}{N}x\cdot k} f_1^{(\nu)}(x) + \sum_{q\in X^*} f_2^{(\nu)}\left(q+\frac{k}{N}\right)\right)$$

$$- \frac{\mu_f([0,\nu^2])}{2}$$

The nonsummable case: Minimizing the reduced energy

Let $f_1^{(\nu)}(x) = \int_{\nu^2}^{\infty} e^{-t|x|^2} d\mu_f(t)$ and $f_2^{(\nu)}(x) = \pi^{\frac{d}{2}} \int_0^{\nu^2} t^{-\frac{d}{2}} e^{-\frac{\pi^2}{t}|x|^2} d\mu_f(t)$

We then have to minimize

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

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

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

We conclude as in the absolutely summable case.

Born's Conjecture: Conclusion

In **[B.-Knüpfer '17]**, we proved:

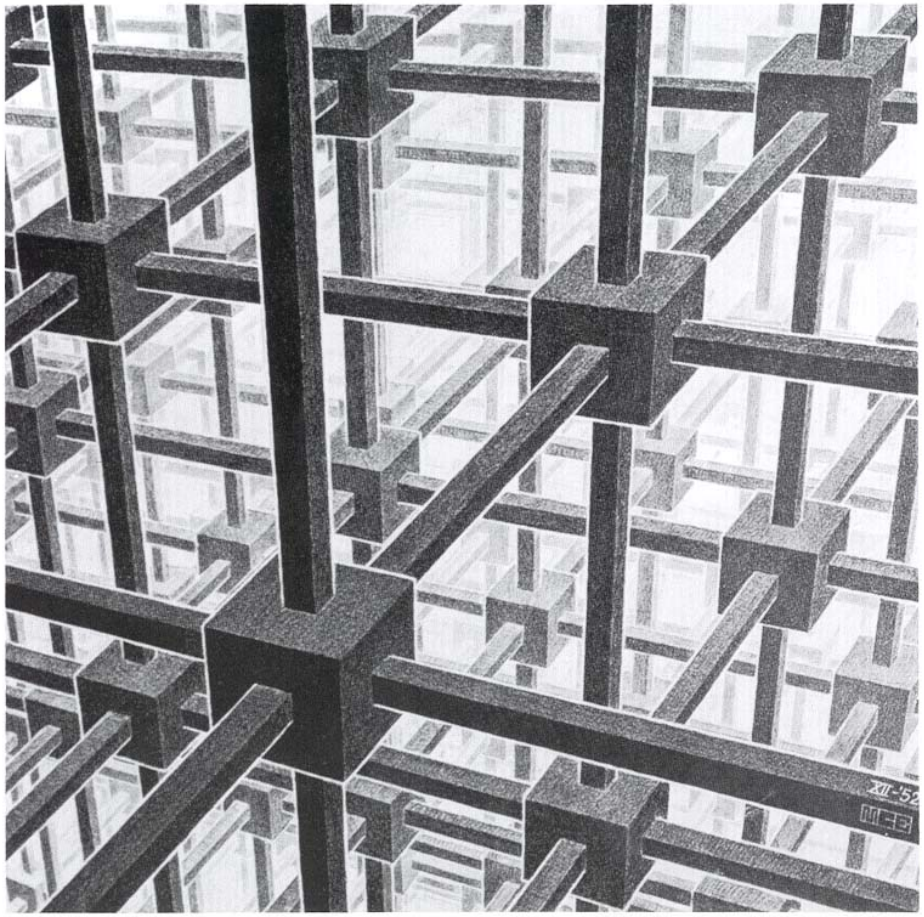
- **Absolute summable f**: **any minimizer** of $\mathcal{E}_{X,f}$ among $\varphi \in \Lambda_N(X)$ such that $\sum_{y \in K_N} \varphi_y^2 = N^d$ **is neutral**, i.e. $\sum_{y \in K_N} \varphi_y = 0$.
- If we know the (at most two) minimizer $z_0 \in \frac{1}{N} X^*$ of $z \mapsto \theta_{X^*+z}(\alpha)$ for any $\alpha > 0$, the **unique** minimizing N-periodic configuration φ^* such that $\varphi_0^* > 0$ and $\sum_{y \in K_N} (\varphi_y^*)^2 = N^d$ is given, for any $x \in X$, by

$$\varphi_x^* = c \cos\left(2\pi x \cdot z_0\right).$$

- For orthorhombic lattices, φ^* is the **alternation of charges** -1 and 1.
- For the triangular lattice, φ^* 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 α-dependence of $\min_{z\in Q}\theta_{X+z}(\alpha)$.



Escher - Cubic space division, 1953.

Thank you for your attention!