From Local to Global Order in Crystals: Rigorous Results

Geometry Days in Novosibirsk
Dedicated to 85th anniversary of
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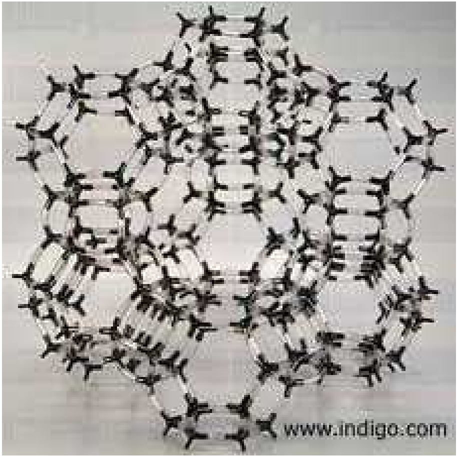
Ideal Crystal; Quartz: Exterior Shape

Quartz (a species of zeolites)

Ideal Crystal; Quartz: Internal Structure



Zeolites have microporous interior structure

Quartz is a species of Zeolites

Definition of a Crystal; Fedorov, 1885

Definition (of crystal)

Let $\mathbb{X}^d$ be space with constant curvature,
G a crystallographic group operating in $\mathbb{X}^d$,
$X_0 \subset \mathbb{X}^d$ a finite point subset: $X_0 = \{x_1, \ldots, x_m\}$,
G-orbit of the set X_0

$$G \cdot X_0 = \cup_i^m G \cdot x_i$$

is called a crystal

Definition (of regular systems)

If $X_0 := \{x\}$, an orbit $G \cdot x$ of a single point is called a regular system.

- A regular system is a particular case of a crystal.

Crystallographic groups

- A subgroup $G \subset Iso(d)$ of isometries is a crystallographic group if
  G is a discrete subgroup of $Iso(d)$
  the space of orbits $\mathbb{X}^d \backslash G$ is compact.

Theorem (Schoenflis: $d = 3$; Bieberbach: $\forall d > 3$; Hilbert XVIII Problem)

Let $\mathbb{X}^d = \mathbb{R}^d$, then a crystallographic group G contains a subgroup T of translations of space with a finite index h: $G = T \cup Tg_2 \cup \ldots \cup Tg_h$.

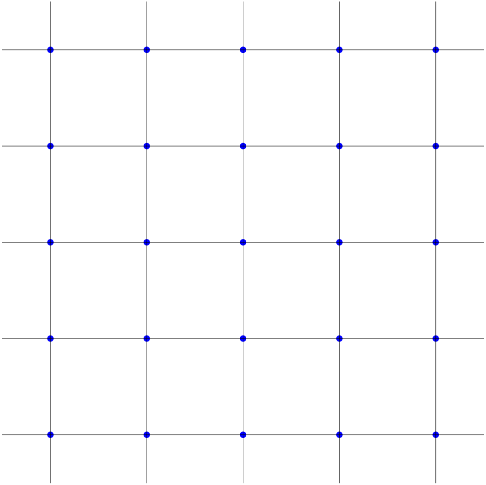
- Due to the Theorem a crystal $G \cdot X_0$ is the union of finite number congruent and parallel lattices

$$G \cdot X_0 = \cup_i^m (T \cdot x_i \cup T \cdot g_2(x_i) \cup \ldots \cup T \cdot g_h(x_i)).$$

- Therefore, a crystal is periodic ("in all d dimensions").

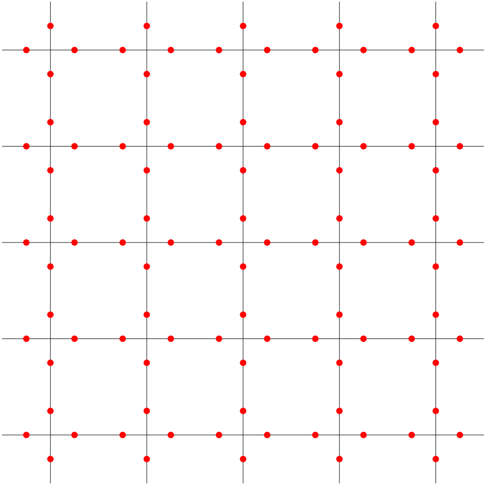
Regular Systems: Example.

Regular system: Lattice



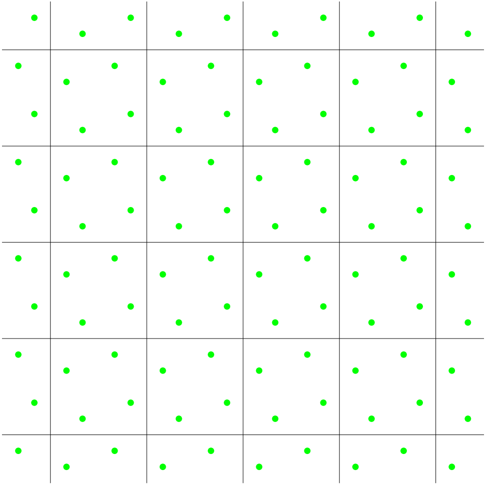
Regular Point Sets. Examples.

Regular system: an orbit with 4 lattices



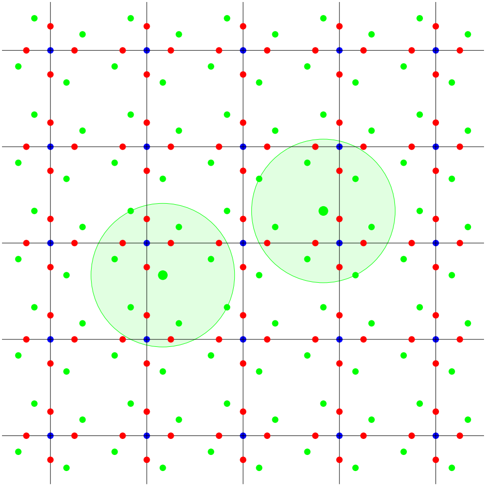
Regular Point Sets. Examples.

Regular system: generic orbit with 4 lattices



Crystal: Example.

Crystal: of 3 regular systems= of 9 lattices



From Disorder to Global Order

- The inner well-ordered structure in crystal appears from amorphous solution under crystallization
- Under crystallization atoms try to bind to the local arrangements with the minimally possible binding energy
- For any two identical atoms minimal energy of local configurations is attained on identical configurations.
- Therefore atoms of the same species try to bind to the pairwise identical local patterns minimizing the energy
- Physists (Pauling, Feynmann) found the following postulate obvious (see Feynmann Lectures on Physics, v. VII): The recurrence in crystal of local identical arrangements implies global periodicity of a crystalline structure.
- However, in quasicrystals (Shechtman, 1982, Nobel Prize, 2011) there is recurrence of local arrangements but NO global order/periodicity at all.

Main Goal of the Local Approach

- Local theory of crystalline structure was (and is) designed: correctly formulate appropriate local conditions and from them **rigorously** derive "the global order".
  to distinct which local arrangments do admit globally ordered extensions and which do not.
- The initiator of the first line was Boris Delone (1890-1980)

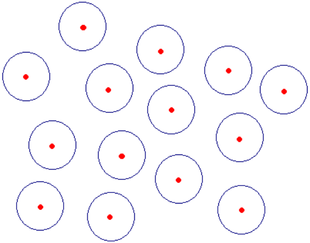
Delone sets

Definition

A point set $X \subset \mathbf{R}^d$ is a Delone set the following conditions hold:
(r) $\exists r > 0$ such that balls $B_x(r)$, (centered at $x \in X$ with radius r) form a packing of space (the balls do not overlap) (discreteness);
(R) $\exists R > 0$ such that balls $B_x(R)$, (centered at $x \in X$ with radius R) do cover all space ($\cup B_x(R) = \mathbf{R}^d$) (no empty holes in X)

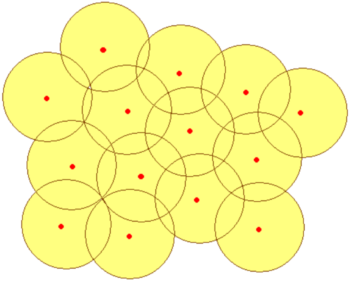
Delone Set: r is a Packing Radius

- Balls centered at pts of X with radius r form packing (do not overlap).



Delone Set: R is Covering Radius

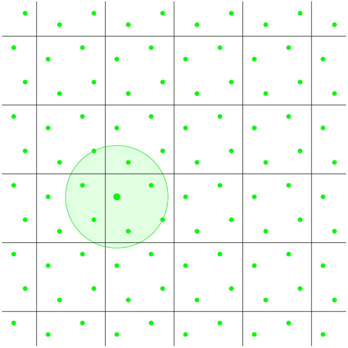
- R-balls centered at points of X cover space $\mathbf{R}^d$



ρ-cluster in a Delone Set

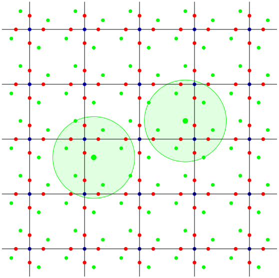
- Given Delone set X, $\mathbf{x} \in X$, and a positive ρ, a ρ-cluster at point $\mathbf{x}$ is

$$C_{\mathbf{x}}(\rho) =: \{\mathbf{x}' \in X \ : \ |\mathbf{xx}'| \leq \rho\}.$$



Enumerative Function

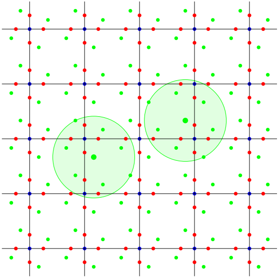
- Given a Delone set X and number $\rho > 0$, set of *rho*-cluster splits into classes of congruent clusters
- the number $N(\rho)$ of classes of ρ-clusters in X is a function of ρ and called *enumerative* function



- Assume that X is a Delone set of *finite type*, i.e. $N(\rho)$ is determined and finite for any $\rho > 0$

Enumerative function and Crystals

- $N(\rho)$ is monotonically non-decreasing, integer-valued function;
- X is regular system $\Leftrightarrow N(\rho) \equiv 1$
- X is crystal with m regular sets $\Leftrightarrow \max_\rho N(\rho) = m$,



Symmetries of a cluster

- Denote by $S_{\mathbf{x}}(\rho)$: $\mathrm{Sym}(C_{\mathbf{x}}(\rho), \mathbf{x})$ the symmetry group of a ρ-cluster.
- Note that $S_{\mathbf{x}}(\rho) \supseteq S_{\mathbf{x}}(\rho')$ if $\rho < \rho'$
- Let $M_{\mathbf{x}}(\rho) := |S_{\mathbf{x}}(\rho)|$ be the order of the group of a cluster $C_{\mathbf{x}}$.
- The function $M_{\mathbf{x}}(\rho)$ is piecewise-constant, non-increasing, integer-valued function. $M_{\mathbf{x}}(\rho) \geq M_{\mathbf{x}}(\rho')$ if $\rho < \rho'$.
- Assume for two points **x** and **x'** its clusters $C_{\mathbf{x}}(\rho)$ and $C_{\mathbf{x}'}(\rho)$ are equivalent. Then the groups of the clusters are conjugate in $Iso(d)$ and $M_{\mathbf{x}}(\rho) = M_{\mathbf{x}'}(\rho)$

Local Criterion for crystals

Theorem (Local Criterion, Dolbilin, Stogrin)

Delone set X is a crystal of m regular systems if (and only if) for some $\rho_0 > 0$ two conditions hold:
(1) $N(\rho_0) = N(\rho_0 + 2R) = m$
(2) for every i-th class ($i = 1, \dots, m$) of ρ-clusters we have:
$M_i(\rho_0) = M_i(\rho_0 + 2R)$,
where $M_i(\rho_0)$ denotes the order of groups of clusters from i-th class.

Some Corollaries

From Local Criterion can be derived that the following theorem

Theorem

There is such a ρ_0 that a Delone set X with parameters r, R is a crystal of m orbits if and only if

$$N(\rho_0) = m,$$

where $\rho_0 = \rho_0(r, R, m, d)$.

Some Corollaries

Close reformulation of the last result gives a representation on the behavior of the enumerative function.

Theorem (Sufficient Conditions, Lagarias, Senechal and N.D.)

Let $X \subset R^d$ be a Delone set with constants (r, R). If for some radius ρ_0 the number $m = N(\rho_0)$ of classes of its ρ_0-clusters satisfies

$$N(\rho_0) < \frac{\rho_0}{CR},$$

where $C = C(R/r, d)$.
Then X is a crystal with exactly m orbits.

- Thus, if the enumerative function $N(\rho)$ at the beginning grows rather slowly then it is bounded for all $\rho > 0$
- Note that for the Penrose quasi-periodic 2D-patterns $N(\rho) \sim \rho^2$

Local criterion for regular systems

The following criterion for regular systems follows from the local criterion for crystals

Theorem (Local theorem, Delone, Dolbilin, Stogrin)

A Delone set is a regular set if and only if for some radius ρ_0 *two conditions hold:*
$N(\rho_0 + 2R) = 1$ *and*
$M(\rho_0) = M(\rho_0 + 2R)$

Corollaries from Local Theorem

Statement

. Assume in X $N(4R) = 1$ and a $2R$-cluster has no symmetry. Then X is a regular System

- $4R$ is precise, i.e. for any $\varepsilon > 0$ the condition $N(4R - \varepsilon) = 1$ does not suffice:
- In any dimension for any $\varepsilon > 0$ there exists a Delone set X (with parameter R) such that $N(4R - \varepsilon) = 1$ but X is not a regular system.
  Moreover, among such non-regular sets with $N(4R_\varepsilon) = 1$ there are such X that function $N(\rho) \sim \rho^2 \to \infty$ as $\rho \to \infty$.

Results for $d = 2$ and $d = 3$

Theorem (Stogrin, Dolbilin)

$d = 2$. $N(4R) = 1 \Rightarrow N(\rho) \equiv 1$, *i.e.* X *is a regular system*

Recall that for any $\varepsilon > 0$ the condition $N(4R - \varepsilon) = 1$ does not suffice:
In any dimension for any $\varepsilon > 0$ there exists a Delone set X (with parameter R) such that $N(4R - \varepsilon) = 1$ but X is not a regular system.

Theorem (Stogrin, N.D)

$d = 3$: $N(10R) = 1 \Rightarrow X$ *is a regular system*

Central Symmetry: Local-Global

- Many natural crystals (e.g., sault NaCl) have locally antipodal structure.

Theorem (N.D.)

Let $X \subset \mathbb{R}^d$ be such that
All 2R-clusters $C_x(2R)$ are centrally symmetrical.
Then the whole X is centrally symmetrical about any $x \in X$

Central Symmetry: Local-Global

Theorem (N.D)

Let $X \subset \mathbb{R}^d$ be such that
All $2R$-clusters $X_x(2R)$ are centrally symmetrical.
Then the whole X is centrally symmetrical about any $x \in X$

Regular Systems

Theorem

Let $X \subset \mathbb{R}^d$ be such that
(1) $N(2R) = 1$,
(2) $2R$-cluster $C_x(2R)$ is centrally symmetrical.
Then X is regular system

!! Compare with $N(4R - \varepsilon) = 1$ is not enough !!

Symmetry of $2R$-clusters $\Rightarrow$ Uniqueness

Theorem (Uniqueness theorem, N.D., A.Magazinov)

Let X and Y be Delone (r, R)-sets and such that
1) all $2R$-clusters are centrally symmetrical;
2) for some $x \in X$, $y \in Y$ $x = y$, $X_x(2R) = Y_y(2R)$.
Then $X = Y$.

Symmetry of $2R$-clusters $\Rightarrow$ Crystal

The uniqueness theorem easily implies the following theorems (just mentioned theorem)

Theorem

Let $X \subset \mathbb{R}^d$ be such that
(1) $N(2R) = 1$,
(2) $2R$-cluster $C_x(2R)$ is centrally symmetrical.
Then X is a regular system

It is important that if even $N(2R) = 1$ is not required the local symmetry implies crystalline structure:

Theorem (N.D., A.Magazinov)

Let $X \subset \mathbb{R}^d$ be such that
$2R$-cluster $C_x(2R)$ for $\forall x \in X$ is centrally symmetrical.
Then X is a crystal

Some of Open Problems

- Prove (or disprove)
  Conjecture: $d = 3$, $N(4R) = 1 \Rightarrow N(\rho) = 1$ for any $\rho > 0$, i.e. X is Regular system.
- $d \geq 4$, prove:
  for any $d \geq 4$ $\exists$ $k(d) > 0$ such that does not depend on r and R and $N(kR) = 1 \Rightarrow N(\rho) \equiv 1$ for any ρ. i.e. X is a regular system
- The most challenging problems:
  $d \geq 2$, find local conditions of X to be a quasicrystal (not a crystal).
  to study conditions for nucleous of crystalline and quasicrystalline structures with this or that kind of symmetry

Дорогой Юрий Григорьевич !

С днем рождения !