Algebraic Description of Coordination Sequences and Exact Topological Densities for Zeolites

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Introduction

The coordination sequence (CS) is a number sequence, in which the *k*−th term is the number of atoms in "shell" *k* bonded to atoms of shell *k*−1. Shell 0 is a single atom, and the number of atoms in the first shell is the conventional coordination number.

The CS was introduced by Brunner & Laves [1] to investigate the topological identity of frameworks and of atomic positions within a framework. It is now routinely used to characterize crystallo−graphic structures and even higher−dimensional sphere packings.

Although it was known that for many zeolites the terms of the CS grow quadratically with *k*, no systematic investigation had been carried out.

Up to 2000 terms have now been calculated for all the zeolites tabulated in [2] and for 11 selected dense SiO_2 polymorphs, and the algebraic structure of these CS's has been analyzed.

In two dimensions the progression of the CS terms is linear with *k*. In analogy to the formula for the circumference of a circle

$$c = 2 \pi r$$

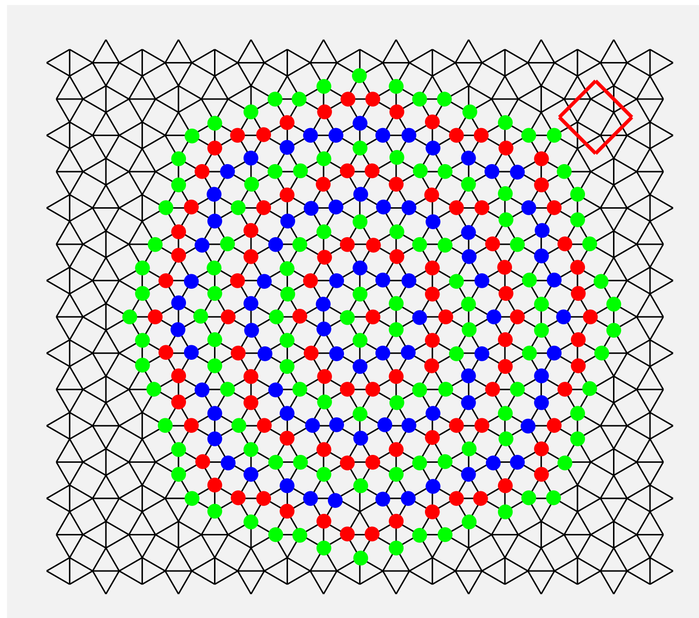
the terms of the CS can be expressed by a periodic set of *p* linear equations

$$N_k = a_i k + b_i \quad \text{for} \quad k = i + p\, n$$

for $i = 1 \ldots p$.

2−Dimensional Example

Plane group *p* 4 *g*
Node at x = (1+sqrt(3))/2, y = 1/2−x



Shell *k*	0	1	2	3	4	5	6	7	8	9	10
Color	red	green	blue	red	green	blue	red	green	blue	red	green
N_k	1	5	11	16	21	27	32	37	43	48	53
$N_k - N_{k-1}$		4	6	5	5	6	5	5	6	5	5

First differences => period length = 3

Fit of N_k to 3 linear equations for $k = 1 \ldots 6$

$$N_k = 16/3\, k - 1/3 \quad \text{for} \quad k = 1 + 3n$$
$$N_k = 16/3\, k + 1/3 \quad \text{for} \quad k = 2 + 3n$$
$$N_k = 16/3\, k + 0 \quad \text{for} \quad k = 3 + 3n$$

=> Exact topological density = 16/3

Recursive decomposition

Initial terms 1 4 6 4 1
Period lengths 3 1

Two Algebraic Descriptions

Recursive decomposition

The terms of the CS are coded into a set of

n_{it} "initial terms" and a set of

n_{pl} "period lengths".

The CS terms N_0 ... N_{k_max} are reconstructed with this simple algorithm:

Copy initial terms to N_0 ... N_{n_it-1}
N_{n_it} ... $N_{k\_max} = 0$
For each period length p
For each $k = p$ ... k_{max}
$N_k = N_k + N_{k-p}$

The recursive decomposition was derived from the "Ordinary Generating Function" [3] description for integer sequences.

Periodic set of quadratic equations

The terms of the CS are expressed by a periodic set of p quadratic equations

$$N_k = a_i\, k^2 + b_i k + c_i \quad \text{for} \quad k = i + p\, n$$

for $i = 1$ ... p.

The "exact topological density", TD, is the mean of the a_i.

TD Determination Strategy

Computation of 100 ... 2000 terms of the CS with a straight−forward (but highly optimized) node−counting algorithm.

Investigation of the second differences => one "period length" for the recursive decomposition.

Determination of the recursive decomposition by means of a brute−force search algorithm.

Computation of a few million terms of the CS and search for periods
=> set of quadratic eqs.
=> TD.

3−Dimensional Example

Zeolite ABW
Space group *I m a m* (74)
Node at x = 0.368, y = 0.379, z = 1/4

Shell k	0	1	2	3	4	5	6	7	8	9	10
N_k	1	4	10	21	36	54	78	106	136	173	214
1. Diff.		3	6	11	15	18	24	28	30	37	41
2. Diff.			3	5	4	3	6	4	2	7	4

Second differences not periodic => b_i <> 0

Fit of N_k to 3 quadratic eqs. for $k = 1$ ... 9

$$N_k = 19/9\, k^2 + 1/9\, k + 16/9 \quad \text{for} \quad k = 1 + 3\, n$$
$$N_k = 19/9\, k^2 - 1/9\, k + 16/9 \quad \text{for} \quad k = 2 + 3\, n$$
$$N_k = 19/9\, k^2 + 0\, k + 2 \quad \text{for} \quad k = 3 + 3\, n$$

=> Exact topological density = 19/9

Recursive decomposition

Initial terms 1 3 6 9 9 6 3 1
Period lengths 3 3 1

The Most Complex Structure

Zeolite EUO
Space Group *C m m a* (67)
10 nodes

Recursive decomposition
Number of initial terms: 224 ... 240
Number of period lengths: 12

Periodic set of quadratic equations
Period length: 140,900,760
TD: 2.619

RAM memory allocated [4]:
3.75 Giga bytes

References

[1] G.O. Brunner & F. Laves; Zum Problem der Koordinationszahl; Wiss. Zeitschr. Techn. Univ. Dresden 20 (1971) 387−390

[2] W.M. Meier & D.H. Olson; Atlas of Zeolite Structure Types, 1992

[3] N.J.A. Sloane & S. Plouffe; The Encyclopedia of Integer Sequences; Academic Press 1995

[4] U. Hollerbach, University of Maryland, USA, private communication