REVISIÓN DE MODELOS Y ALGORITMOS DE PREDICCIÓN DE REDES CRISTALINAS

Trabajo de grado de Ingeniería Física
Iván David Buitrago Torres
Dirigido por Ph.D. Elisabeth Restrepo

PCM Computational Applications

Justification

- Knowledge and understanding of the methods
- Prediction of structures unknown to the date
- Meta-Stable Structures (Optimization of physical properties)
- Cost reduction

Objectives

- General:
- Make a review of the methods that exists and are being developed for the prediction of crystal structures.

- Specifics:
- Carry out a bibliographical search of the methods developed for the prediction of crystal structures.
- Explain conceptually and systematically the process used in each method

Crystal Structure Prediction

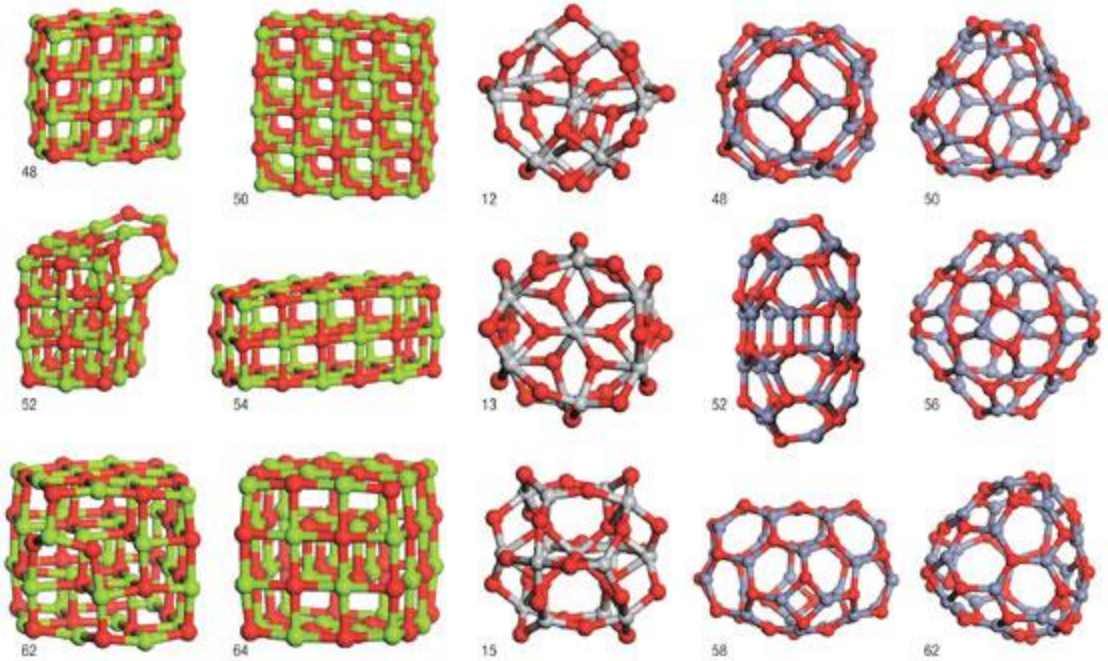
- Prediction =/= Simulation

Prediction: Ab Initio Calculations in order to obtain structures.

Simulation: Experimental Structural Data in order to obtain physical properties.

Crystal Structure Prediction

- Jhon Maddox, 1988: "One of the continuing scandals in the physical sciences is that it remains in general impossible to predict the structure of even simplest crystalline solids from a knowledge of their chemical composition."



Taken from Crystal structure prediction from first principles, Scott M. Woodley & Richard Catlow

Crystal Structure Prediction

- Crystal structure prediction by evolutionary algorithms and direct search methods (Diploma thesis) Bc. Oto Kohulák. Univerzita Komenského v Bratislave:

Thermodynamics: Functions of free energy: Gibbs, Enthalpy, Helmholtz, etc…

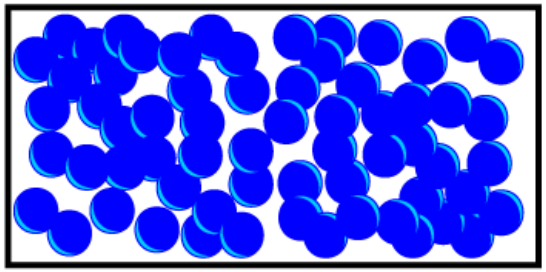
Minimum Energy = Stable Structure = Thermodynamical Equilibrium

Crystal Structure Prediction

- Why not one by one?

- We can try to reach minimum by fixing every position but…
- 10^{23} particles per cm^2

1 mole of sodium



has 6.023 X 10 ^{23} atoms

equipmentexplained.com

Taken from http://chemistryhungergames.weebly.com/uploads/8/8/4/9/8849208/190572_orig.gif

Crystal Structure Prediction

- Then what?…

- Stablish energy function, number of particles, and chemical/thermodynamical parameters.
- Use energy term as objective function.
- Apply Algorithms.

Crystal Structure Prediction

- Constrained and unconstrained Gibbs free energy minimization in reactive systems using genetic algorithm, Adrián Bonilla-Petriciolet.
- At constant temperature T and pressure P, for c multi component and π multi phase system:

$$G = \sum_{j=1}^{\pi} \sum_{i=1}^{c} \eta_{ij} \mu_{ij}$$

$$\eta = number\ of\ moles\ of\ component\ i\ in\ phase\ j$$
$$\mu = chemical\ potential\ of\ component\ i\ in\ phase\ j$$

- «variables are based on the transformation of physical compositions, restrict the solution space to the compositions that satisfy stoichiometry requirements, and also reduce the dimension of the composition space by the number of independent reactions satisfying the Gibbs phase rule."

$$F = C - P + 2$$

Crystal Structure Prediction

- Crystal structure prediction by evolutionary algorithms and direct search methods (Diploma thesis), Bc. Oto Kohulák
- «To have sufficient precision for our calculations, we cannot use classical potentials, on the other hand full quantum mechanical calculations with multielectron wave functions are too time consuming. So we must perform quantum calculations in clever way."

$$H = -\sum_e \frac{\hbar^2}{2m_e}\Delta_{r_e} - \sum_i \frac{\hbar^2}{2m_i}\Delta_{r_i} + \frac{1}{2}\sum_{e\neq e'} \frac{e^2}{|\boldsymbol{r}_e - \boldsymbol{r}_{e'}|} + \frac{e^2}{2}\sum_{i\neq i'} \frac{Z_i Z_{i'}}{|\boldsymbol{r}_i - \boldsymbol{r}_{i'}|} + \frac{e^2}{2}\sum_{e,i} \frac{Z_i}{|\boldsymbol{r}_e - \boldsymbol{r}_i|},$$

$$n(\boldsymbol{r}) = \sum_i \int_\sigma g_i |\psi_i(\boldsymbol{r}_\sigma), |^2,$$

Global Optimization Algorithms

Global optimization algortithms, Thomas Weise

The optimization is a branch of applied mathematics

$$f: X \rightarrow Y, f \in F$$

Classification of optimization methods:

By operation mode:

- Deterministics
- Stochastic
- Heuristic
- Metaheuristic

By its properties:

- Online
- Offline

Some definitions

Solution candidates/phenotypes:

$$x \in X$$

Solution space S:

$$X^* \subseteq S \subseteq X$$

Optimal Set:

$$x^* \in X^*$$

Search space / Genome:

$$g \in G$$

Gene: Distinguishable unities in genotypes

Some definitions

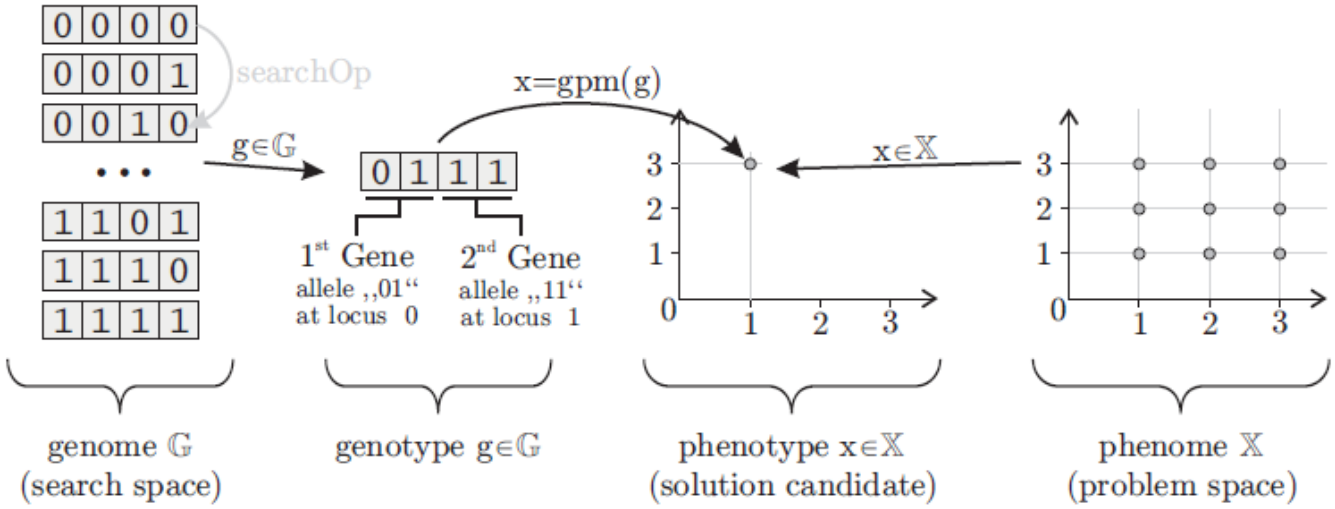
Search Operations:

searchOp allow to solve a given problem in a defined set with different arities

Genotype/Phenotype Mapping: Phenomena to Math interpretation

$$gpm: G \rightarrow X$$
$$\forall g \in G \exists x \in X: gpm(g) = x$$

An optimization problem is well defined if X, F, G, Op and gpm are known



Some definitions

- Objective space: Codomain of all objective functions

$$F = \{f_i : X \to Y_i : 0 < i < n, Y_i \in R\} \to Y = Y_1 x Y_2 \dots x Y_n$$

Fitness: Messure of «good» or «bad» (Only have meaning during the process)

$$v(x) \in V : X \to V, V \in R^+$$

Individual:

$$p.x = gpm(p.g)$$

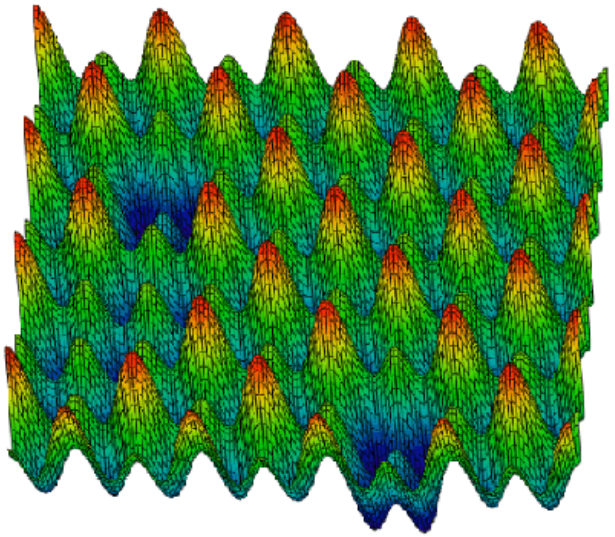
Some definitions

Population:

$$Pop \in GxX: \forall p(p.g, p.x) \in Pop \rightarrow p.x = gpm(p.g)$$

Problem Landscape: Maps X to a Probability

$$\Phi: XxN \rightarrow [0,1] \in R^{+}$$



Taken from http://news.princeton.edu/uploads/296/image/model_landscape.gif 10/03/2017

Some definitions

- Optimization Algorithm: Transformation

Will find x^* if:

- searchOp is partially ordered
- gpm is surjective

$$(X, F, SearchOp, G, gpm) \rightarrow \Phi$$

$$\exists x_i^* \in X \rightarrow \lim_{t \rightarrow \infty} \Phi(x_i^*, t) = 1$$

Multiobjective functions

- Weighted sums:

$$g(x) = \sum_i \omega_i f_i(x)$$

Pareto optimization: Domination

$$x_1 \vdash x_2 \leftrightarrow \forall i: 0 < i < n \rightarrow \omega_i f_i(x_i) \leq \omega_i f_i(x_i)$$
$$\wedge \exists j: j < n \rightarrow \omega_j f_j(x_j) \leq \omega_j f_j(x_j)$$

Multiobjective functions

Pareto optimal: Element which is not dominated by any other.

$$x^* \in X^* \leftrightarrow \nexists\, x \in X : x \vdash x^*$$

Prevalence comparator function: Generates Optimal Set X^*, compares elements of X

$$(x_1 \succ x_2)\ if\ cmp_F(x_1, x_2) < 0$$

x_1 prevails over x_2

$$x^* \in X^* \leftrightarrow \nexists\, x \in X : x = x^* \wedge x \vdash x^*$$

Evolutionary Algorithms

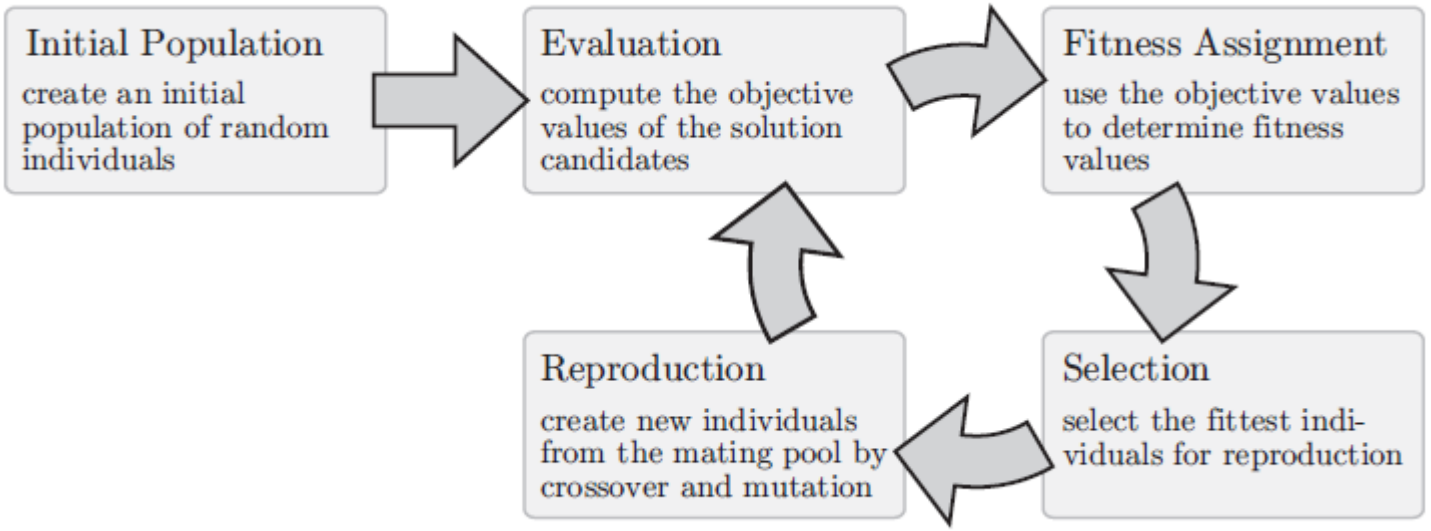
- Based in 10 statements made by Charles Darwin in his 1859 book «On the origin of the species»

1. Big fertility -> More offspring
2. Population is constant
3. Food is limited but stable
4. Individuals fight for food -> Fight for survival
5. Not 2 identical individuals in sexual reproductions
6. Variations affect fitness hence survival
7. Some variations are hereditary
8. Less fitness, less offspring
9. Individual survive and reproduce, transmit features
10. Species change along time

Evolutionary Algorithms

- Search space is all DNA chains.
- Fitness is measured depending of objective function.

Evolutionary Algorithm Scheme



Evolutionary Algorithm Scheme

- Initial population (Pop) are individuals p with gnome p.g
- Each individual p.x is evaluated in f
- Comparation between evaluations with cmpf set fitness
- In reproduction phase p.g genomes are combinated randomlly through a searchOp and offspring is combines with Pop to form next generation.
- Termination criterion is evaluated

Evolutionary Algorithm Implementation

Algorithm 2.1: $X^\star \longleftarrow \text{simpleEA}(\text{cmp}_F, ps)$

Input: cmp_F: the comparator function which allows us to compare the utility of two solution candidates
Input: ps: the population size
Data: t: the generation counter
Data: Pop: the population
Data: $Mate$: the mating pool
Data: v: the fitness function resulting from the fitness assigning process
Output: $X^\star$: the set of the best elements found

```
1  begin
2      t ⟵ 0
3      Pop ⟵ createPop(ps)
4      while ¬terminationCriterion() do
5          v ⟵ assignFitness(Pop, cmp_F)
6          Mate ⟵ select(Pop, v, ps)
7          t ⟵ t + 1
8          Pop ⟵ reproducePop(Mate)
9      return extractPhenotypes(extractOptimalSet(Pop))
10 end
```

Implementation

- USPEX (Universal Structure Predictor: Evolutionary Xtallography)

Unexpected Stable Stochiometries of Sodium Chlorides.

Weiwei Zhang, Artem Oganov.

Unexpected Stable Stoichiometries of Sodium Chlorides

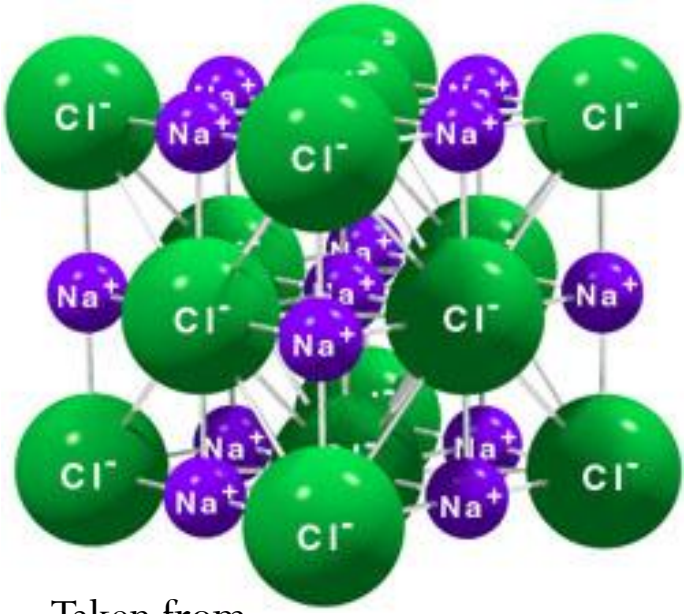
Weiwei Zhang,[1,2*†] Artem R. Oganov,[2,3,4*†] Alexander F. Goncharov,[5,6] Qiang Zhu,[2] Salah Eddine Boulfelfel,[2] Andriy O. Lyakhov,[2] Elissaios Stavrou,[5] Maddury Somayazulu,[5] Vitali B. Prakapenka,[7] Zuzana Konôpková[8]

Sodium chloride (NaCl), or rocksalt, is well characterized at ambient pressure. As a result of the large electronegativity difference between Na and Cl atoms, it has highly ionic chemical bonding (with 1:1 stoichiometry dictated by charge balance) and B1-type crystal structure. By combining theoretical predictions and diamond anvil cell experiments, we found that new materials with different stoichiometries emerge at high pressures. Compounds such as Na_3Cl, Na_2Cl, Na_3Cl_2, $NaCl_3$, and $NaCl_7$ are theoretically stable and have unusual bonding and electronic properties. To test this prediction, we synthesized cubic and orthorhombic $NaCl_3$ and two-dimensional metallic tetragonal Na_3Cl. These experiments establish that compounds violating chemical intuition can be thermodynamically stable even in simple systems at nonambient conditions.

NaCl

- FCC Structure
- Stable
- Lower Energy State

Taken from http://www.mspbs.gov.py/dvent/wp-content/uploads/2016/02/Sal.png

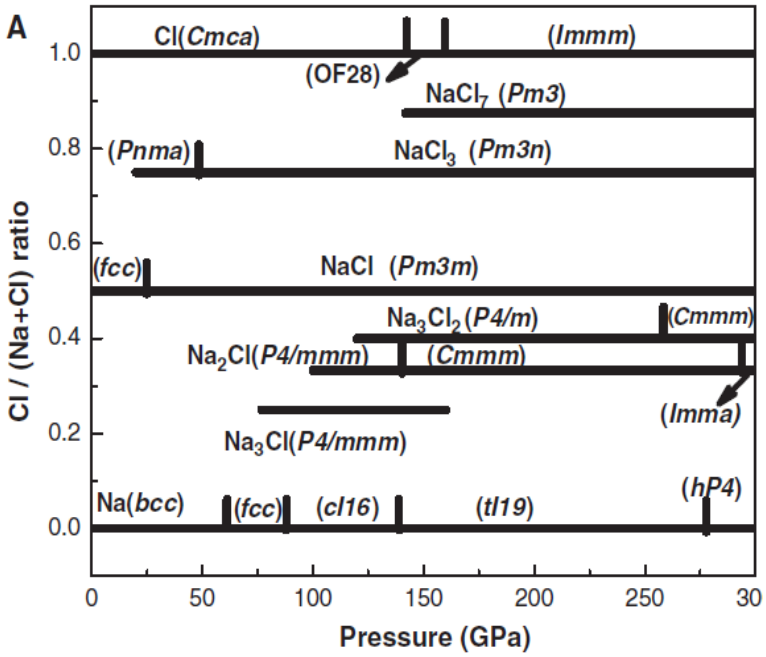


Taken from http://moorechemistry.weebly.com/solvation-process.html

NaCl

- At high temperatures and high pressures, apportation of energy will be bigger than inner energy of the system.

$$G = U + \rho V - TS$$



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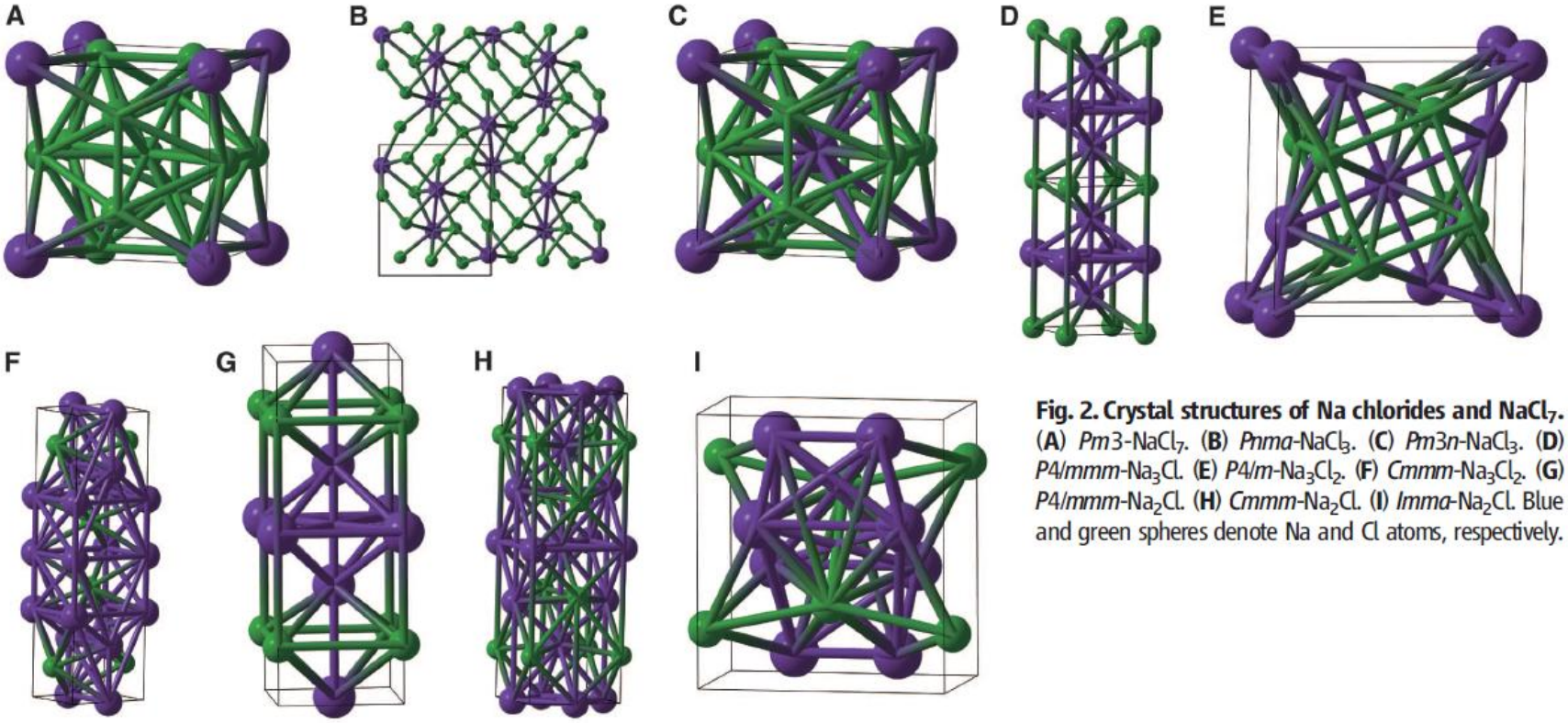

Fig. 2. Crystal structures of Na chlorides and $NaCl_7$. (**A**) *Pm*3-$NaCl_7$. (**B**) *Pnma*-$NaCl_3$. (**C**) *Pm*3*n*-$NaCl_3$. (**D**) *P*4/*mmm*-Na_3Cl. (**E**) *P*4/*m*-Na_3Cl_2. (**F**) *Cmmm*-Na_3Cl_2. (**G**) *P*4/*mmm*-Na_2Cl. (**H**) *Cmmm*-Na_2Cl. (**I**) *Imma*-Na_2Cl. Blue and green spheres denote Na and Cl atoms, respectively.

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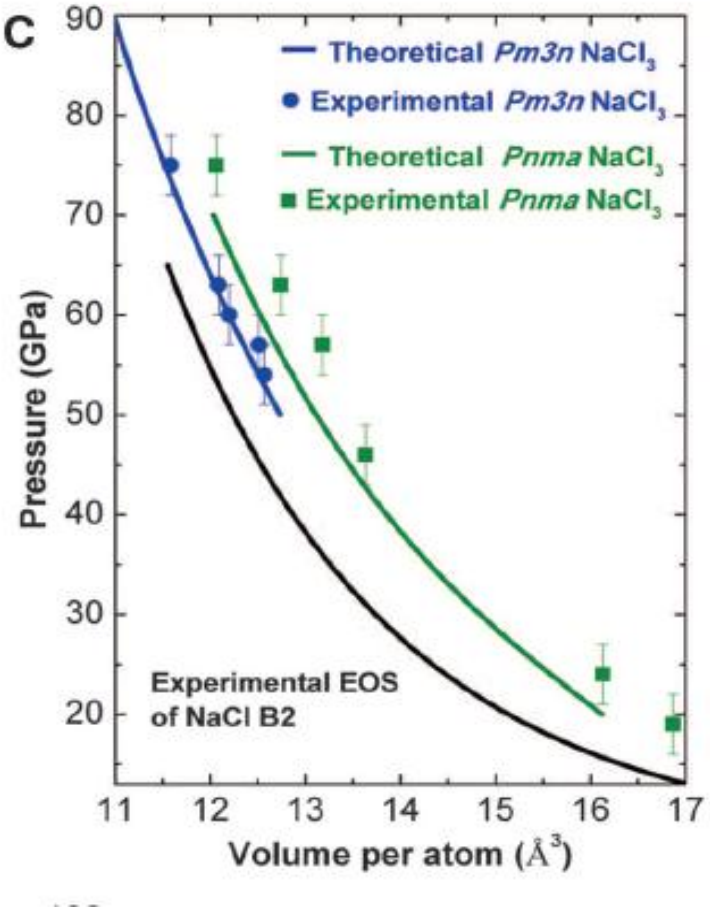
NaCl



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What is next?

- Determine the conceptual bases and the algorithmic structure of another global optimization methods like Simulated Annealing, Particle Swarm Optimization, etc.
- Study the physical variables that describe the behaviour of nanoparticle systems, to stablish the global application of these algorithms to different systems.
- Review results obtained with these algorithms.
- Program some of these algorithm at short range for empiric tests.

THANK YOU!