Application of optimization methods for modelling of close packings crystal structures

K. K. Abgaryan*

*Dorodnicyn Computing Center RAS, kristal83@mail.ru

In this paper, we formulate a closed-form mathematical problem describing the search of possible crystal structures conforming to a given chemical formula. First, we define the concept of stability of a crystal substance in the general case.

Let the chemical formula of a compound for example, $A_iA_j = AB$, $i, j = \overline{1,n}$ (for example, NaCl, be given). Using the algorithms described in ([1], [2]) all possible symmetry groups corresponding to this formula can be found.

Consider the well-known rigid sphere (ion atomic radii) model. In this model, the stability criterion of a crystal structure with a given crystal-chemical formula requires that the spheres (atoms) in the structure be closely packed (the packing closeness ρ must be within the range $0.56 \le \rho \le 0.74$ and the crystal structure must correspond to a minimum of the potential energy (see [1], [3], [4]).

In the three-dimensional space, denote by (X_A^i, Y_A^i, Z_A^i) the coordinates of the center of the sphere A_i.

Denote by $A = \{(X_A^i, Y_A^i, Z_A^i)\}$ and $B = \{(X_B^i, Y_B^i, Z_B^i)\}$ the classes of indistinguishable atoms (spheres), $i = \overline{1,n}$.

Definition 1 *The atoms (spheres) $A_i(B_j)$ ($i = \overline{1,k}$, $k \le n$) belong to the class of indistinguishable atoms (spheres) $A(B)$ if all of them are at the equivalent Wyckoff positions and denote the same chemical element, that is, the radius of the i-th sphere $r_{A_i}(r_{B_i}) =$* const *for every i-th sphere, where $i = \overline{1,k}$, $k \le n$.*

For every pair of spheres i, j (independently of whether or not they belong to the same equivalence class) with the corresponding radii $r(i)$ and $r(j)$, the condition

$$R(i,j) \ge r(i) + r(j) \tag{1}$$

must be satisfied, where $R(i,j)$ is the distance between the centers of the spheres i and j.

Due to the symmetry of the crystal, in order to find an optimal structure (in terms of the packing closeness [2]), it is sufficient to consider a finite set of all the pairs of spheres $\{(i,j)\}$ such that i runs over the set of nonequivalent positions (spheres) within the same elementary cell and j is the set of spheres' positions in this and in the adjacent cells.

Consider the cubic symmetry. Let the coordinates of the center of the sphere A be given by a radius vector beginning at the origin:

$$\overline{r_A} = \overline{x_A}a + \overline{y_A}b + \overline{z_A}c \tag{2}$$

here, a, b, and c are the constants of the lattice,

$$\rho(\overline{r_{Ai}}, \overline{r_{Bj}}) = \sqrt{(X_{Ai} - X_{Bj})^2 - (Y_{Ai} - Y_{Bj})^2 - (Z_{Ai} - Z_{Bj})^2} \tag{3}$$

distance between possible pairs of sphere (A_i, B_j) belonging to different equivalence classes A and B.

Let

$$\rho(A,B) = \min_{Ai \in A,\, Bj \in B} \rho(\overline{r_{Ai}}, \overline{r_{Bj}}). \tag{4}$$

If $A \equiv B$, then $i \ne j$

It is clear that

$$\rho(A,B) \ge r(A) + r(B) \tag{5}$$

where $r(A)$ and $r(B)$ are the radii of any of the spheres belonging to the classes A and B, respectively.

Define

$$\xi = \max_{A,B}\{(r(A) + r(B))/\rho(A,B)\}, \quad 0 \le \xi \le 1. \tag{6}$$

For the lattice constants a, b, and c, we have

$$\overline{a} = \overline{a}'\xi, \overline{b} = \overline{b}'\xi, \overline{c} = \overline{c}'\xi.$$

Volume of an elementary cell

$$V = (\overline{a}, \overline{b}, \overline{c}) = \xi^3 |\overline{a'} \quad \overline{b'} \quad \overline{c'}|. \tag{7}$$

Therefore, the optimization problem is formulated as follows: find all the local minima V^0 in the minimax problem ([1]):

$$V^0 = \min_{\{(X_A, Y_A, Z_A) \in W\}} \left\{ \left(\max_{A,B}[r(A) + r(B)]/\rho(A,B)\right)^3 \times \right.$$

$$\times \left| \begin{array}{ccc} a'_x & a'_y & a'_z \\ b'_x & b'_y & b'_z \\ c'_x & c'_y & c'_z \end{array} \right| \Bigg\}, \tag{8}$$

where

$$W = \{\{(X^i, Y^i, Z^i)\}/X_i = K_i^1 a,\ Y_i = K_i^2 b,$$
$$Z_i = K_i^3 c,\ 0 \le K_i^1 \le 1,\ 0 \le K_i^2 \le 1,\ 0 \le K_i^3 \le 1\}. \tag{9}$$

This is a minimax problem subject to coupled constraints. The difficulty is that simultaneously three minimax problems subject to coupled constraints must be solved in the general case.

From the local minima of the volume of the Bravais parallelepiped V^0, we calculate the packing closeness for the given chemical-crystal formula as

$$\rho = \frac{4}{3}\pi \frac{\sum\limits_{A^i} \upsilon(A_i) r^3(A_i)}{V^0}. \tag{10}$$

Here, the sum is taken over the classes of nonequivalent atoms, and $\upsilon(A^i)$ is the number of atoms in the class A_i per an elementary cell.

Note that the values of V^0 depend on the system of radii (ionic or atomic) in which the calculations are performed.

The packing closeness determined for each local minimum of the objective function (which is generally found by formula (10)) is the parameter used to reject the structures that cannot exist. For example, it is known that the value of ρ for crystal solids is within the range

$$0.56 \le \rho \le 0.74. \tag{11}$$

In the organization of the computation process in the general case, all the possible configurations (sets of coordinates of the spheres' centers) that locally minimize a given objective function for the prescribed parameter $P \in [0.5, 0, 74]$ are sought (in the general case, $\min V$ is sought (see (10)).

A special approach based on the well-known simulation annealing method was developed for solving this problem. The idea of this approach is to discretely move the spheres according to one of the two algorithms (or their combinations), so as to minimize the given objective function (8) for the given parameter $P \in [0.5, 0.74]$ with allowance for conditions (6) and (9).

References

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