ALGORITHM FOR REALISTIC MODELING OF GRAPHITIC SYSTEMS

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An algorithm for molecular dynamics simulations of graphitic systems using realistic semiempirical interaction potentials of carbon atoms taking into account both short-range and long-range contributions is proposed. Results of the use of the algorithm for a graphite sample are presented. The scalability of the algorithm depending on the system size and the number of processor cores involved in the calculations is analyzed.

Keywords: *MOLECULAR DYNAMICS, GRAPHITE, COVALENT BONDS, DISPERSION INTERACTION, PARALLEL COMPUTING.*

1. INTRODUCTION

Graphite is a laminated material, which is widely used both in everyday life (for example, in pencils) and in high-tech applications as a solid lubricant in devices with movable components and as a working substance in moderators of neutrons of nuclear reactors [1-3]. Investigation of graphite properties has a rather long history, and on the early stages it was mainly targeted on the description of its macroscopic characteristics. Discovery of new graphitic systems, such as carbon nanotubes and graphene, led to the fact that the investigation focus and search for possible applications was shifted from the macroscopic scales to nanolevel due to the corresponding characteristic sizes of the mentioned materials [4-6].

In the theoretical description of the properties of low-dimensional systems, development of phenomenological models is often found to be too complicated problem. This is conditioned by the strongly pronounced atomistic nature of nanodimensional objects, which cannot be neglected, by introducing some averaged parameters. Therefore, atomistic simulation, in particular, by the method of classical molecular dynamics (MD) became an indispensable tool of the theoretical study of low-dimensional systems.

The type of the potential, which describes interatomic interactions, is the key factor in classical MD. It depends on the formulated problem, in particular, on the atomic composition and dimensions of the considered system, and on the results which should be obtained [7-9]. When constructing the model, one always has to choose an optimal ratio of the following competing factors: description accuracy of the system behavior, its sizes (simulation duration), and computing time, which is spent on the numerical solution of the problem. Tendency to describe exactly all interactions in the system cau-

ses an increased complexity of the computation and long-time calculations. This leads to the fact that it is possible to describe in detail only small systems, which contain a little amount of atoms, or, probably, larger systems but on shorter times. Simplified consideration of interactions, contrariwise, decreases computational cost and gives the possibility to calculate for larger systems and long time intervals. However, the last approach can omit some contributions, which though can seem insignificant, but neglecting them it is possible to obtain the wrong result or miss some effects. Thus, there is a need to develop approaches, which would allow to perform shorter (over the machine time) calculations keeping sufficient detail in system description. Because of the development of parallel computing during last years, there is a possibility to accelerate calculations not due to the decrease in the detail of system description, but due to the optimization of algorithms and using supercomputers [10-13].

In the given work for a realistic model of graphitic systems, which takes into account the basic types of interactions, we propose an algorithm, which allows (keeping high degree of detail in interaction description) to carry out calculations using standard supercomputers for sufficiently large systems.

2.   INTERATOMIC INTERACTIONS OF GRAPHITIC SYSTEMS

2.1 Main contributions

Interactions with different scale values of spatial action are the feature of graphitic systems.

Carbon atoms in nanotube or in graphene are connected by very strong short-range covalent bonds, whose radius of action is of the order of 0,2 nm [14]. Strength of the bonds conditions high frequency values of phonon vibrational modes. For example, the mode frequency along graphene layer in graphite sample is about 46,3 THz [15]. This fact forces to use in calculations a small time step (about 0,1 fs) that is one order less than the typical value, which is used in the simulation of liquids. This leads to the substantially less simulation duration.

During interaction of carbon atoms from different graphitic systems, for example, two nanotubes, nanotube-graphene (graphite surface), graphene layers in graphite, the long-range attractive Van der Waals (VDW) interaction with the radius of action of the order of 1 nm [14] plays a key role (dispersion interaction gives the main contribution to the VDW interaction). However, it is not a unique one as the experiments and theoretical investigations based on ab initio calculations [1, 16, 17] show. Appreciable contribution to the bonding energy of graphene layers gives a repulsive interaction conditioned by the overlap of electron densities (orbitals) between weakly interacting subsystems (for example, different graphite layers). Though the given overlap is small, one should not neglect its energy, since, for example, just it determines layer packing in different forms of graphite (the so-called α-graphite with the AB layer packing or turbostatic graphite with an arbitrary packing) [1, 16, 17].

Thus, the model focused on a realistic description of the behavior of graphitic systems should take into account all three contributions to the system potential energy. We consider mathematical expressions used for semiempirical potentials of the specified interactions in our model. In the given work we study graphite sample, therefore, in the description of contributions to

the potential energy we will use the term "interlayer interaction" for non-covalent component. However, it is necessary to remember that the mentioned potential and algorithm can be used for other graphitic systems, for example, carbon nanotubes.

2.2 Functional forms of the interaction potentials

A few semiempirical potentials [10, 18-21] were proposed during last 20 years in order to describe covalent bonds. In spite of the relative complexity in comparison with harmonic potentials [18], the Brenner potential [19, 20] is the most popular in classical MD. It allows to model sufficiently exactly the covalent bonds not only of graphitic systems, but other allotropic forms of carbon, and hydrocarbonates as well. Recently, application of a new ReaxFF (reactive force field) potential [21] is often found. This potential, using a classical approach, allows to describe systems with the accuracy close to the accuracy of the quantum chemistry methods. However, use of ReaxFF requires larger computational cost than the Brenner potential does.

In our model we use the following Brenner potential:

$$V_B = \sum_i \sum_{j>i} \left[V^R(r_{ij}) - \bar{b}_{ij} V^A(r_{ij}) \right]. \tag{1}$$

Here functions $V^R(r_{ij})$ and $V^A(r_{ij})$ are the paired-additive interactions, which represent all interatomic repulsions (between ion cores, etc) and attraction between valent electrons, respectively. The value of r_{ij} is the distance between pairs of closest atoms-neighbors i and j; $\bar{b}_{ij}$ is the bond-order term representing the bond type between i and j atoms and including many-particle effects, which are necessary for the correct description of bonding in hydrocarbonates. Expressions for functions involved in (1) can be found in [22]

The force acting on the atom k due to the covalent bond with other atoms is determined as follows

$$\mathbf{f}_k = -\frac{\partial V_B}{\partial \mathbf{r}_k}. \tag{2}$$

Expressions for the force (2) obtained using (1) can be found in [23]. We do not represent them here because of their cumbersome form.

In the given work for intermediate interactions we use the RDP (registry-dependent potential) proposed by Kolmogorov, which has the form

$$V\left(\mathbf{r}_{ij}, \mathbf{n}_i, \mathbf{n}_j\right) = e^{-\lambda(r_{ij}-z_0)} \left[C + f\left(\rho_{ij}\right) + f\left(\rho_{ji}\right) \right] - A\left(\frac{r_{ij}}{z_0}\right)^{-6}. \tag{3}$$

Here $\lambda = 36{,}29$ nm^{-1}, $z_0 = 0{,}334$ nm, $C = 3{,}030$ meV, $A = 10{,}238$ meV. Potential contains the proportional to r^{-6} VDW attraction and the exponentially decreasing repulsion due to the overlap of the wave functions of electrons from different layers. To take into account the spatial directivity of the overlap, we have introduced the function f, which drops rapidly with the transverse distance ρ (see Fig. 1)

$$f\left(\rho\right) = e^{-(\rho/\delta)^2} \sum C_{2n} \left(\rho/\delta\right)^{2n}, \tag{4}$$
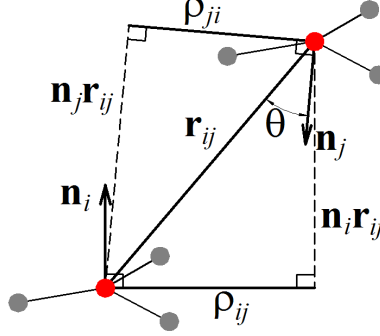
Fig. 1 − Illustration of the quantities involved in formulas (3)-(6)

where $C_0 = 15{,}71$ meV, $C_2 = 12{,}29$ meV, $C_4 = 4{,}933$ meV, $\delta = 0{,}0578$ nm.

The value of ρ is determined by the distance r_{ij} between pairs of atoms i and j from different layers and the vector $\mathbf{n}_k$ ($k = i$, j), which is the normal to the sp^2 plane near the atom k

$$\rho_{ij}^2 = r_{ij}^2 - (\mathbf{n}_i \mathbf{r}_{ij})^2, \quad \rho_{ji}^2 = r_{ij}^2 - (\mathbf{n}_j \mathbf{r}_{ij})^2. \tag{5}$$

In the present work $\mathbf{n}_k$ is calculated as the "local" normal, i.e. as the mean value of three normalized vector products of the radius-vectors traced from the atom k to its closest neighbors. The given technique corresponds to the RDP1 in the work [16]. For the long-range VDW term the cutoff distance is equal to $r_c = 2{,}7 \, z_0 = 0{,}9018$ nm. The layer bonding energy E_{il} is calculated as follows

$$E_{\text{il}} = \sum_i \sum_{j>i} V\left(\mathbf{r}_{ij}, \mathbf{n}_i, \mathbf{n}_j\right). \tag{6}$$

In **(6)** summation is done over the carbon atoms of two adjacent layers and function V is defined by the formula **(3)**.

The force acting on a carbon atom due to the interlayer interactions is determined by the formula similar to **(2)** with replacement of V_B by E_{il}. The differentiation gives

$$\mathbf{f}_i = -\frac{\partial E_{\text{il}}}{\partial \mathbf{r}_i} = -\sum_i \sum_{j>i} \frac{\partial V}{\partial \mathbf{r}_i} = -\sum_i \sum_{j>i} \frac{dV}{dr} \mathbf{e}_{ri}, \tag{7}$$

$$\frac{dV}{dr} = e^{-\lambda(r-z_0)} \left[-\lambda \left(C + f(\rho_{ij}) + f(\rho_{ji}) \right) + \left. \frac{df}{d\rho} \right|_{\rho_{ij}} \frac{d\rho_{ij}}{dr} + \left. \frac{df}{d\rho} \right|_{\rho_{ji}} \frac{d\rho_{ji}}{dr} \right] + \frac{6A}{z_0} \left(\frac{r}{z_0} \right)^{-7} \tag{8}$$

$$\frac{df}{d\rho} = \frac{2\rho}{\delta^2} e^{-(\rho/\delta)^2} \left[C_2 - C_0 + \left(\frac{\rho}{\delta} \right)^2 \left(C_4 \left[2 - \left(\frac{\rho}{\delta} \right)^2 \right] - C_2 \right) \right], \tag{9}$$

$$\frac{d\rho_{ij}}{dr} = \left[r^2 - \left(\mathbf{n}_i \mathbf{r} \right)^2 \right]^{-0.5} \left[r - \left(\mathbf{n}_i \mathbf{r} \right) \cos \angle \left(\mathbf{r}, \mathbf{n}_i \right) \right], \tag{10}$$

$$\frac{d\rho_{ji}}{dr} = \left[r^2 - \left(\mathbf{n}_j \mathbf{r} \right)^2 \right]^{-0.5} \left[r - \left(\mathbf{n}_j \mathbf{r} \right) \cos \angle \left(\mathbf{r}, \mathbf{n}_j \right) \right]. \tag{11}$$

In (7) $\mathbf{e}_{ri}$ denotes the unit vector along the direction of the radius-vector $\mathbf{r}_{ij}$, which connects atoms i and j from different layers. Symbol $\angle(\mathbf{r}, \mathbf{n}_i)$ designates the angle between radius-vector and local normal.

3. THE MODEL AND THE ALGORITHM

In the present work we consider α-graphite with the AB layer packing. The sample consists of two or three layers (Fig. 2) and contains 16 or 24 hexagons of carbon atoms ("combs") along both axes x and y. Periodic boundary conditions are applied to the sample in the xy-plane. Atoms interact in conformity with the laws described in the previous section. Equations of motion are integrated by the Verle method [9, 10] with the time step of 0,1 fs. The given system represents the basis for modeling of surface phenomena and foliation of graphite sample in the works [22, 24, 25].
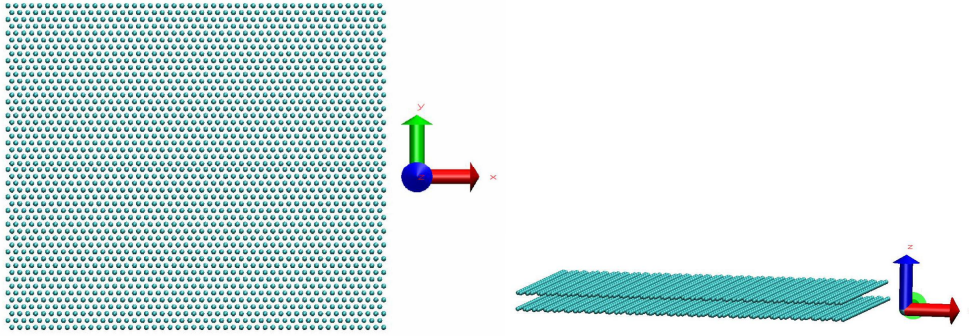

Fig. 2 – Top and lateral views of one of the studied systems

As known, substantial computational cost (in comparison with simple paired potentials) is required for calculation of the forces derived from the Brenner potential due to many-particle nature and complexity of the bond-order term $\overline{b}_{ij}$ in (1) [10, 23]. Simple enumeration of the neighbors is found to be extremely ineffective, and to decrease calculation time one usually uses the cell linked lists and parallelization based on domain decomposition [10, 23].

The cell linked list method allows to organize information about atomic position in such a way that the required computational cost is found to be proportional to the number of atoms N (and not to the square of the number of atoms as in the case of enumeration of all neighbors) [9, 10, 23]. The idea of the method consists in the following. As it was noted, covalent bonds have small radius of action, of the order of 0,2 nm. Therefore, for the Brenner potential the cutoff radius $r_{Bc} = 0,2$ nm is introduced. If interatomic distance is more than this value, it is considered that the covalent bond is absent. The modeling region is divided into cubic cells, whose edge length exceeds the mentioned cutoff radius r_{Bc} (see Fig. 3, the left figure). Then, if atoms are attributed to the cells, proceeding from their current coordinates, it is obvious that interactions are possible only between atoms either from the same cell or from the adjacent cells. If these conditions do not hold, atoms should be positioned, at least, at the distance of the cutoff radius. Organization of the indexes of atoms in each cell into linked lists allows to achieve proportionality between computing time and number of atoms N. We have note, a bypass

of the cells according to a certain rule is performed during calculation. In our algorithm there is scanning of the cells by the way marked by arrows in Fig. 3 (on the left) for the given cell m. The given bypass we will call the long cycle for the cell m.
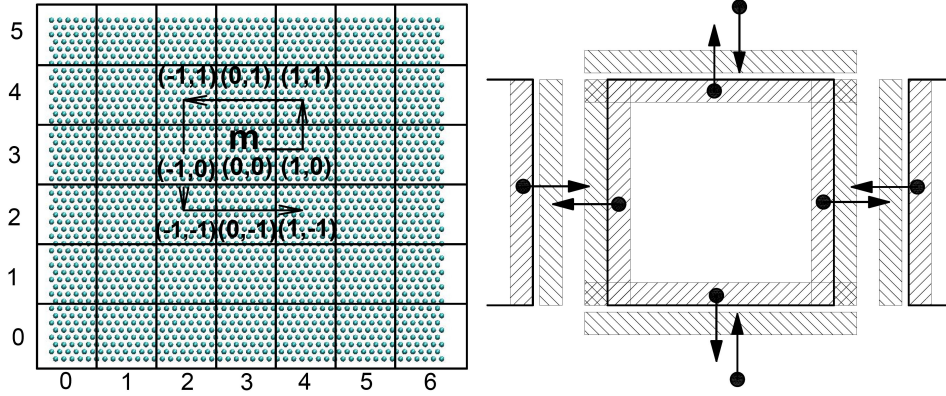
Fig. 3 − *Schematic illustration of the cell discretization of modeling region and cell scanning along the long pass in the xy-plane (on the left); principle of the domain decomposition (on the right)*

However, even use of the cell list does not usually allow to perform calculations for sufficiently large systems. Therefore, often there is a necessity to use parallel computing and supercomputers, where calculations are flowing parallel on some cores. The most popular approach for parallelization of the MD code for supercomputers with distributed memory is the so-called domain decomposition, which was also used in the present work. Its essence is in the following [9, 10, 23]. The modeling region is divided into subregions, each of which is assigned to one processor or processor core (see Fig. 3, on the left). All atoms positioned in the given subregion at some time belong to the corresponding processor. When atom moves between subregions, all variables connected with this atom are explicitly transferred from one processor to another. There is a saving of memory, as well as communications necessary for the transfer of information about atoms, since a rather small amount of atoms makes such movements during one time step. A more important thing is that if comparatively many atoms are in the region and if the short-range potential is used, the major part of the interactions will take place between atoms in the subregion, and a rather small one − between atoms from the adjacent subregions. To accommodate the latter, copies of coordinates of atoms, which are close to any boundary of subregion, before computation of interactions are also transferred to the processor governing the adjacent subregion. The given atoms are often called the virtual ones or atoms-copies. This transfer of information also requires small fraction of atoms and communications. In whole, communication channels with high transmission capacity and small delays, i.e. fast net, are required for the efficiency of the domain decomposition method. Details of the code realization can be found in the works [9, 10].

Presence of the short-range and long-range interactions in graphic systems is a certain difficulty for an optimal realization of the code. This is

conditioned by the fact that in the given case for each type of interactions its own cutoff radius is required. Therefore, when using the cell method, cells of different sizes are necessary. Moreover, presence of normals in the RDP makes it inherently many-particle and complicates calculation of interactions. The mentioned factors condition the necessity of the development of a special algorithm for the calculation of interactions. In the present work we propose one of the algorithms, in which we use cells of two sizes: with the edge of 0,2 nm for the Brenner potential and for the calculation of normals, and with the edge length d defined by the formula

$$d = \sqrt{r_c^2 - z_0^2} \,, \tag{12}$$

where $z_0 = 0{,}334$ nm is the equilibrium distance between layers of α-graphite; $r_c = 2{,}7\, z_0 = 0{,}9018$ nm is the cutoff distance for the VDW interaction. We will call large cells the Kolmogorov ones and small cells for the calculation of normals − the cells of normals. Some preliminary actions, such as cell discretization of modeling region, determination of a true number of Kolmogorov cells (without copies) and widths of Kolmogorov cells and cells of normals, are required before calculation.

Calculation of the forces acting on atoms in graphite consists in the calculation of covalent interactions determined by the Brenner potential and the VDW contribution and contribution from the overlap of orbitals from RDP. Calculation of covalent forces is performed by the algorithm form work [23] irrespective of two other contributions. For the latter the Algorithm 1 given below was used.

Algorithm 1

I For all Kolmogorov cells:
   1. To obtain index $m1$ of the Kolmogorov cell;
    2. Long cycle for the column cells, where the cell $m1$ is positioned, in the xy-plane:
       i) to determine index $m2$ of the adjacent Kolmogorov cell;
       ii) for each atom i from the cell $m1$:
          a) to determine index $m1Norm$ of the cell of normal for atom i;
          b) long cycle for the cell of normal $m1Norm$:
            - to obtain index $m3$ of the cell of normal;
            - by enumeration of each atom k from the cell $m3$ to find three closest neighbors of the atom i;
            - to calculate radius-vectors from the atom i to three closest neighbors and the corresponding normalized vector products. To find their mean value − there is the desired normal $\mathbf{n}_i$;
          b) the end;
          c) for each atom j from the cell $m2$:
            1) to determine distance r_{ij};
            2) if atoms i and j from different layers then:
               A) to determine index $m2Norm$ of the cell of normal for atom j;
               B) long cycle for the cell of normal $m2Norm$:
                 - to obtain index $m3$ of the cell of normal;
                 - by enumeration of each atom k from the cell $m3$ to find three closest neighbors of the atom j;

- to calculate radius-vectors from the atom j to three closest neighbors and the corresponding normalized vector products. To find their mean value − there is the desired normal $\mathbf{n}_j$;
B) the end;
C) to determine relative positions of the layers and the corresponding directions of normals;
D) to calculate bonding energy of the layers and forces by the formulas **(6)-(11)**;
  2) the end;
    c) the end;
     ii) the end;
  2. End of the long cycle over the column cells;
I End of the cycle over all Kolmogorov cells.

We note, the given algorithm can be used both for sequential calculations and for parallel ones, since it does not include evident data transfer between processors. All communications occur by the cycle of the force calculation (before it and after it). In the case of parallel code one should pay attention on the handling of periodic boundary conditions. More detailed discussion of this question and example of the code can be found in [9].

4. RESULTS

The foregoing algorithm is implemented in C. MPI specification was used for parallelization, the code debugging was performed using Microsoft MPI, the final code version was compiled and assembled with the MPICH2 realization [26]. Calculations were carried out on the beowulf SumDU cluster [27], which consists of 12 nodes. Each node contains CPU Intel® Core™ 2 Duo E6600, 2,4 GHz, net 1Gbit Ethernet.
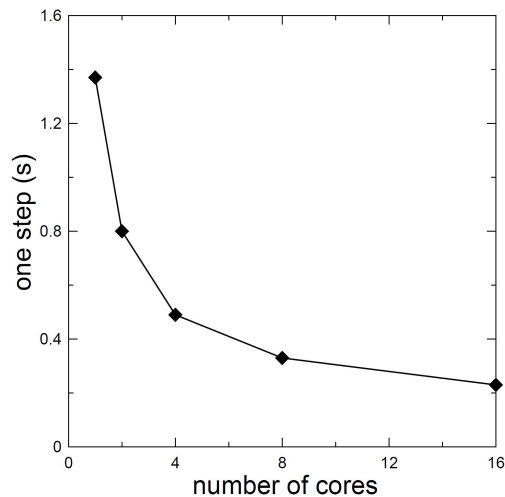
Fig. 4 − Duration of calculation of one time step depending on the number of processsor cores

In Fig. 4 we present the dependence of the calculation time of one time step for a graphite sample containing **16 × 16** "combs" in the layer along the

x and y axes, **4608** atoms in all. It is seen that time decays nonlinearly approaching to saturation, when number of processors exceeds **16**. We can notice that scalability of calculations has a sufficiently small value. This is conditioned by the low transmission capacity of the net of 1Gbit Ethernet cluster, as well as by a small size of the system that leads to the increased costs for the data transfer in comparison with duration of calculations produced by each core.

Analysis of the data from Table **1** shows that duration of calculation is mainly defined not by general number of atoms in system but by amount of layers, since calculation time of interlayer interactions increases very fast with the number of layers.

Table 1 − *Duration of calculation of one step for different systems*

Number of "combs" along x	Number of "combs" along y	Number of layers	N	Calculation of one time step (s)
16	16	2	3072	0,120
16	16	3	4608	0,233
24	24	2	6912	0,185
24	24	3	10368	0,360

As time dependences of the bonding energy of layers E_{il} and distances between layers d_{il} presented in Fig. 5 show, these quantities fluctuate near the values about **42 meV** and **0,333 nm**, respectively. The same results were obtained for different sized systems. The given numbers are close to the experimental values [16]. However, there is **15%** difference between the bonding energy and the value **48 meV** obtained theoretically for the RDP in [16]. Discrepancy can be explained by a finite cutoff distance used in our calculations for the VDW contribution. Moreover, in [16] a static sample was considered, while dynamic bonds in our model lead to the thermal oscillations of atoms, which condition fluctuations of normals that also can be the reason of the mentioned mismatch of values.
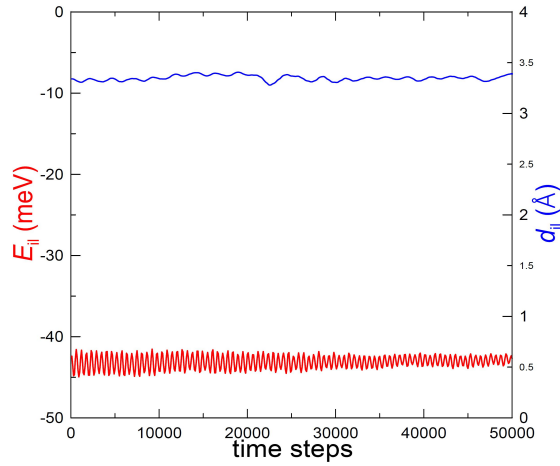
Fig. 5 − *Time dependences of the bonding energy of layers E_{il} and interlayer distance d_{il} for a system, which contains 24 × 24 "combs" along the x and y axes and consists of two layers*

5. CONCLUSIONS

In the work we propose an algorithm for the calculation of interactions in graphitic systems. The algorithm takes into account all main contributions to the potential energy, is grounded on the cell linked list method, and provides the possibility of parallelization based on the domain decomposition. Calculations on the beowulf cluster showed sufficiently low scalability, which is probably connected with the latency of network communications of the cluster. The calculations also imply that with the increase in the number of layers in graphitic sample the main computational load is due on the determination of the long-range contribution to the bonding energy of layers. In a whole, the algorithm can be used for various graphitic systems, and examples of its application for the investigation of graphitic sample layering can be found in the works [22, 24, 25].

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