Algorithm for constructing full-atomic models of X- and T-shaped seamless junctions between single-walled carbon nanotubes

G. V. Savostyanov, D. S. Shmygin[†]

[†]shmygin.dmitriy@gmail.com

Saratov State University, 83 Astrakhanskaya St., Saratov, 410012, Russia

Modeling the formation of junctions between single-walled carbon nanotubes (SWCNTs) requires large computational resources, which makes it difficult to obtain a large statistical sample of such models, which is necessary to solve a number of problems, in particular, studying the electronic conductivity of materials based on SWCNTs. The need for a statistical sample is due to the fact that there can be many variants of possible junctions between SWCNTs, and the properties of such junctions can be different, taking into account the possible contribution of each defect to the junction conductivity. To simplify obtaining of statistical sampling of junction models, a special algorithm is developed. It allows us to significantly reduce time to build full-atomic models of X- and T-shaped seamless junctions between SWCNTs of different chiralities. Within the framework of the created algorithm, carbon surface formation is modeled by adding carbon atoms in the region with unsaturated bonds in stages, followed by optimization of the mutual arrangement of atoms by molecular dynamics using empirical potentials to describe the interaction between atoms. The created algorithm is implemented in SeamMaker software package developed in Python and C++. To create a statistical sample, it is necessary to indicate the chirality of the connected SWCNTs (moreover, the junction of tubes of different chiralities is permissible) and the type of junction of interest (X- or T-shaped). Full-atomic models constructed using the proposed algorithm can be used to study the influence of the topology of complex branched carbon structures on their mechanical and electroconductive properties.

Keywords: single-walled carbon nanotubes, X- and T-shaped seamless junctions, full-atomic model, structural defects.

Алгоритм построения полноатомных моделей X- и Т-образных бесшовных соединений между одностенными углеродными нанотрубками

Савостьянов Г. В., Шмыгин Д. С.[†]

Саратовский национальный исследовательский государственный университет им. Н. Г. Чернышевского, ул. Астраханская, 83, Саратов, 410012, Россия

Моделирование процесса образования соединений между одностенными углеродными нанотрубками (ОУНТ) требует больших вычислительных ресурсов, что затрудняет получение большой статистической выборки подобных моделей, необходимой для решения ряда задач, в частности, исследования электронной проводимости материалов на базе ОУНТ. Необходимость статистической выборки обусловлена тем, что вариантов возможных соединений между ОУНТ может быть много, причем свойства таких соединений могут быть различны, учитывая возможный вклад каждого дефекта в проводимость соединения. Для упрощения получения статистической выборки моделей соединений разработан специальный алгоритм, позволяющий значительно сократить время построения полноатомных моделей X- и Т-образных бесшовных соединений между ОУНТ различной киральности. В рамках созданного алгоритма осуществляется моделирование образования углеродной поверхности путем поэтапного добавления атомов углерода в области с ненасыщенными связями с последующей оптимизацией взаимного расположения атомов методом молекулярной динамики с использованием эмпирических потенциалов для описания взаимодействия между атомами. Используемый при разработке алгоритма подход может быть обобщен для построе-

ния полноатомных моделей различных структур, содержащих углеродные поверхности сложной формы. Созданный алгоритм реализован в программном пакете SeamMaker, разработанном на языках программирования Python и C++. Для статистической выборки необходимо указать киральность соединяемых ОУНТ (причем допустимым является соединение трубок разных киральностей) и тип интересующего соединения (X- или T- образное). Построенные с помощью предложенного алгоритма полноатомные модели могут быть использованы для исследования влияния топологии сложных разветвленных углеродных структур на их механические и электропроводящие свойства.

Ключевые слова: одностенные углеродные нанотрубки, X- и T-образные бесшовные соединения, полноатомная модель, структурные дефекты.

1. Introduction

During the synthesis of single-walled carbon nanotubes (SWCNTs), a large amount of material is obtained containing randomly arranged carbon nanotubes [1,2]. As is known, individual SWCNTs have unique electronic properties, due to which materials with high electrical conductivity are created on their basis [3]. Moreover, in arrays of randomly oriented CNTs, the contacts between them have a high (up to several MΩ) [4] electrical resistance due to the tunneling nature of the electronic conductivity between individual nanotubes [5]. An important task in developing materials based on SWCNTs is to minimize the mass fraction of nanotubes while maintaining high electrical conductivity. So, for example, when creating conductive composite materials for medical purposes [6], the density of SWCNTs must be minimized considering their possible toxicity [7]. Obviously, in the presence of covalent junctions between SWCNTs, the value of the contact resistance will decrease significantly; however, the resistance of the contacting nanotube itself will increase due to a violation of the atomic structure in the contact area. The formation of such junctions is possible, in particular, by irradiating an array of randomly oriented nanotubes with a laser [8].

When junctions are formed between nanotubes, topological defects, such as pentagons, heptagons, etc., are always present in the contact area. Despite the presence of defects in the considered models of junctions, it is usually assumed that the coordination number for each atom is three, as well as for ideal nanotubes consisting of hexagons. This corresponds to seamless connections between SWCNTs. Such junctions differ in the shape and number of nanotubes participating in them [9]. In a number of works, junctions between two nanotubes [10], three [11,12], four [13,14] were considered.

For a detailed study of the properties of junctions between SWCNTs by computational modeling methods, it is necessary to construct full-atomic models of junctions. The direct construction of such models or their preparation using molecular dynamics and Monte Carlo methods [14] are complex and time-consuming processes, while for a more precise study it is necessary to take into account a wide variety of combinations of nanotubes of various diameters and chiralities. Thus, in most works on this subject, researchers are limited to several specific models of junctions [12,13]. The solution to the problem of constructing a non-planar graphene-like surface was proposed in [15]. In this paper, an approach based on surface triangulation is proposed for constructing graphene surfaces containing defects — pentagons and heptagons. This approach can be used to create a simply connected surface and requires improvements to create a surface close to cylindrical. The CoNTub program can now be used to construct symmetric Y-shaped junctions between nanotubes [16], however, its capabilities do not allow asymmetric connections of three nanotubes, for example, T-shaped junctions, as well as junctions of more than three nanotubes. To fully solve the problem of constructing seamless junctions between nanotubes, the corresponding algorithm was created and implemented, and it is described in this paper.

2. Methods and Approaches

The algorithm for automatically constructing full-atomic models of seamless X- and T-shaped junctions between SWCNTs of different chirality is based on the application of an original approach, which consists in simulating the formation of a carbon surface by a gradual addition of carbon atoms to areas with unsaturated bonds, followed by optimization of the mutual arrangement of system atoms by the molecular dynamics method using empirical potentials for describing hydrocarbons.

In order to speed up and control the formation of a junction between SWCNTs, the classical molecular dynamics method was modified by adding an external attractor force field to the so-called supporting surface (Fig. 1a), on which the structure is growing (Figs. 1b, c). To construct the supporting surface, the auxiliary Procedure 1 is used.

2.1. Procedure 1

The supporting surface is represented in the memory of a computer in the form of sets of triangles at two levels of detail (B and M sets in Fig. 2). The need for a two-level presentation will be explained later in the description of Procedure 2.

Without loss of generality, we consider the procedure for constructing a supporting surface using the example of a T-shaped junction between two SWCNTs (SWCNT-A is vertically oriented, SWCNT-B is horizontally oriented and contains a hole opposite SWCNT-A (see Fig. 2 a):

1. Selection of two groups of boundary atoms in the form of rings $ring_1$ and $ring_2$, the proposed centers of growth of the structure (marked in red in Fig. 2 a):

• the $ring_1$ group corresponds to the atoms of the lower edge of the SWCNT-A, having only two covalent bonds;

• the $ring_2$ group corresponds to SWCNT-B atoms, which have only two covalent bonds and are not edge atoms.

2. Building of closed interpolation curves passing through the atoms of the selected boundary rings (blue lines in Fig. 2 a):

• calculation of geometric centers of C_1 and C_2 of rings $ring_1$ and $ring_2$;

• translation of atomic coordinates belonging to the ring$_1$ and ring$_2$ groups, into a cylindrical coordinate system, the Z axis of which connects points C$_1$ and C$_2$;

• construction of interpolation functions depending on the angular coordinate in a cylindrical coordinate system defining closed curves.

3. Building of set B (Fig. 2 b):

• adding vertical segments between rings ring$_1$ and ring$_2$ by connecting pairs of points belonging to different interpolation curves and having the same angular coordinates in the used cylindrical coordinate system;

• adding a diagonal to each quadrangle formed by adjacent vertical segments;

• adding two resulting triangles to the set (adding Cartesian coordinates of vertices and external normals).

4. Building of set M (Fig. 2 c):

• uniform addition of a given number of nodal points on each of the constructed vertical segments;

• adding horizontal segments connecting pairs of nodal points belonging to adjacent vertical segments and having the same number;

• adding diagonal lines in quadrangles to obtain a triangulated surface.

2.2. Attractor to the supporting surface

The modeling of carbon surface growth is carried out via the modified molecular dynamics method, the basis of which is the numerical solution of Newton's equations of motion:

$$\frac{d^2\vec{r}_i(t)}{dt^2} = -\nabla_i U(\vec{r}_1,...,\vec{r}_N) + \vec{F}_{ext}^i, \qquad (1)$$

here an external force $\vec{F}_{ext}^i$ is added to the original formula, which ensures the attraction of atoms to the supporting surface. The reactive empirical bond-order potential (REBO) for hydrocarbons is used as the interatomic interaction potential U [17]. The choice of this potential is associated with its relatively low computational complexity and the ability to simulate the dynamic formation and destruction of covalent bonds during molecular dynamics simulation. The potential energy of a system has the following form (from REBO potential):

$$U_{REBO} = \sum_{i \neq j} f_{ij}(V_R(r_{ij}) + b_{ij}V_A(r_{ij})), \qquad (2)$$

where V_R — repulsion energy, V_A — attraction energy f_i — switching function, smoothly decreasing potential to zero
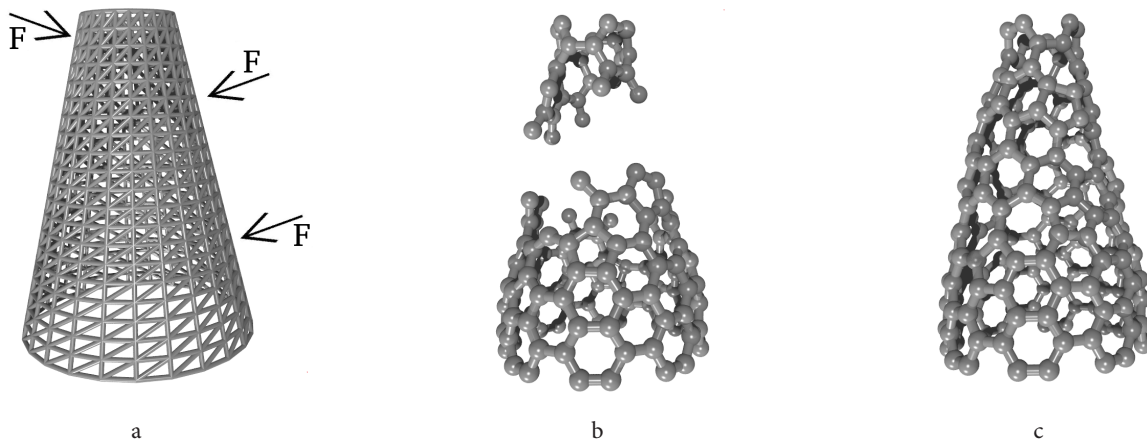

Fig. 1. A network defining a surface in the shape of a truncated cone (a), the process of building a junction between two SWCNTs of different chirality (b), the constructed junction between SWCNTs of different chirality (c).
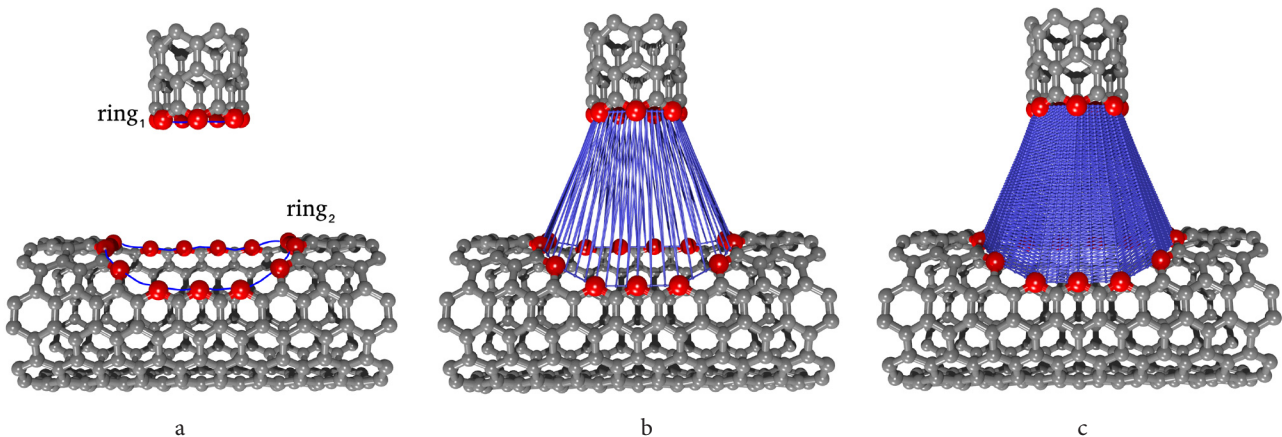

Fig. 2. (Color online) Building a support surface for a T-shaped junction between SWCNTs: Edge rings ring$_1$ and ring$_2$, obtained by constructing a three-dimensional interpolation curve (blue line) passing through the boundary atoms (marked in red) of the full-atomic SWCNT model (a), Set B representing the triangulated supporting surface at the first level of detail (b), Set M representing a triangulated supporting surface at the second level of detail (c).

at large distances between atoms (>2 Å), b_{ij} — bond order, determining the nature of the interaction of two atoms (attraction and repulsion), depending on the neighbouring atoms of atoms i and j. The formulas for finding these quantities are described in the original work of Brenner [17] and implemented in the Kvazar software package [18], on the basis of which the algorithm proposed in this work was developed.

The attractor to the supporting surface, which is used in common with the molecular dynamics method, is set using the constraining force in the following form:

$$\vec{F}_{ext} = kd^2\vec{e}, \qquad (3)$$

where k is the empirically selected coefficient of 10^{-8} H/Å², d — distance from atom to supporting surface, $\vec{e}$ — unit vector from atom to supporting surface (see Fig. 3). Procedure 2 is used to calculate d.

2.3. Procedure 2

The calculation of the distance between the atom and the supporting surface is as follows:

1. Using the Moller-Trumbor algorithm [19], which is known and applied in computer graphics, the distances from the atom beyond the surface to the triangles from set B on the supporting surface are calculated.

2. The nearest triangle T_1 from set B, is determined and it uniquely defines the vertical face of the supporting surface.

3. A subset M' of triangles M is constructed. Triangles belong to the vertical face containing T_1, as well as two adjacent to the first faces.

4. The nearest triangle from M' is determined, the shortest distance from the atom beyond the surface to the triangle is calculated, and the projection of the point on the supporting surface is found (see Fig. 3).

2.4. Algorithm for constructing full-atomic models of X- and T-shaped seamless junctions between SWCNTs

An original algorithm for constructing a junction between SWCNTs within the modified molecular dynamics method (1)-(3) is as follows:

1. Determination of the set of atoms A (marked in red on Fig. 4 a), with a coordination number equal to 2.

2. If the set A is empty, add atoms to the set A with a coordination number of 1.

3. If the set A is empty, complete the construction and go to step 11 (see Fig. 4 c).

4. The construction of the subset A' of the set A using a random number generator so that the nearest distance between each pair of atoms is greater than the distance D_0 (D_0 is selected experimentally and is about 5 Å).

5. Adding additional carbon atoms near the carbon atoms from the set A' (marked in blue in Fig. 4 a).

6. Optimization of the position of added atoms under the external force using molecular dynamics with dissipation [20].

7. The molecular dynamics simulation of the movement of all atoms added at this stage under the external force with the thermostat algorithm at temperature T which is selected empirically and ranges from 300 – 600 K [21].

8. Re-optimizing the positions of all added atoms (see Fig. 4 b).

9. Exclusion from consideration of atoms that located beyond the boundary of the calculated region and are more
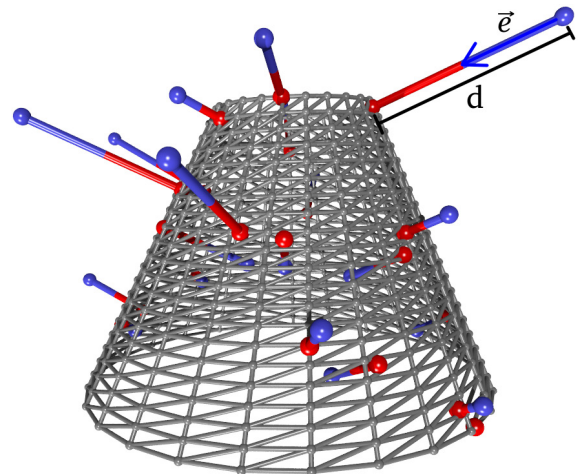

Fig. 3. (Color online) The distance and direction that determine the force of attracti on of atoms to the supporting surface. Blue spheres represent carbon atoms outside of supporting surface, and red spheres correspond to surface points closest to given atoms (projections of atoms to the surface).
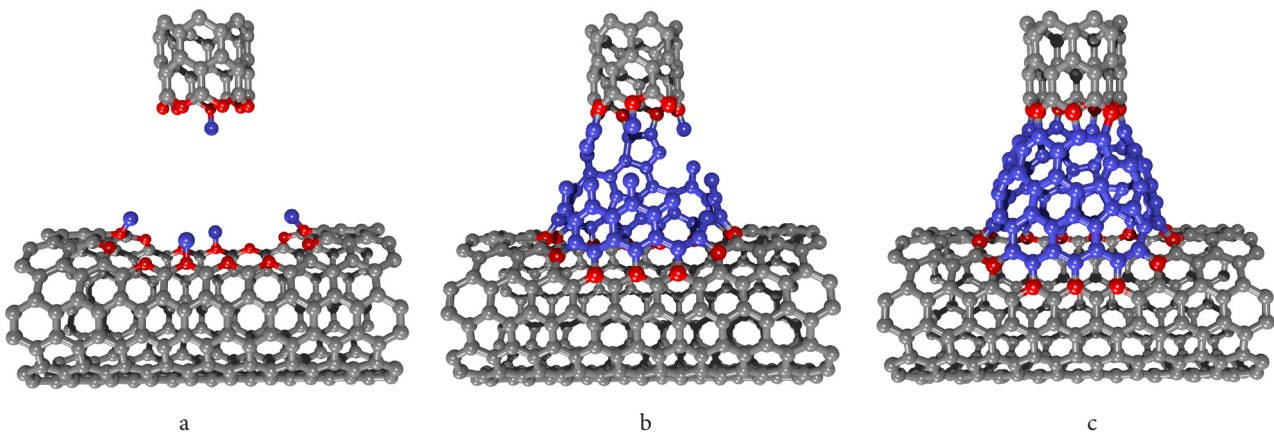

Fig. 4. (Color online) Construction of the junction between two SWCNTs: selection of atoms with a coordination number equal to 2 and completion of the 3rd bond by adding one carbon atom (a), the intermediate stage of construction (b), the constructed junction (c).

than 2 Å away from the supporting surface, as well as atoms that form triangles or quadrangles.

10. Go to item 1.

11. Optimization of the positions of atoms from the joint region without taking into account external force [20].

To build an X-shaped junction, the described procedure is repeated twice, where for the second time, instead of the lower SWCNT-B, a T-shaped junction is used (see Fig. 5).

3. Software implementation of the algorithm

The SeamMaker program which implements the developed original algorithm for constructing full-atom seamless X- and T-shaped junctions between SWCNTs was developed in the Python and C++ programming languages using the Boost. Python library [22] based on the Kvazar software package [18]. When implementing the algorithm, the numpy [23] and scipy [24] libraries were also used, in particular, the scipy. interpolate module was used to construct a curve defining the boundaries of the supporting surface (Procedure 1). SeamMaker is a console application that automatically builds a given number of models of X- or T-shaped junctions between SWCNTs of a given chirality.

To start building a T-shaped connection, the user only needs to specify the chiralities of the first and second SWCNTs, the name template for the output file, and the number of structures that are necessary to obtain. The boundary rings $ring_1$ and $ring_2$ are automatically detected. The atoms of the

SWCNT-B, which fell into the projection of the cylinder SWCNT-A, are removed from the SWCNT-B. The diameter of the cylinder exceeds the diameter of the SWCNT-A by 10%. The atoms of the lateral surface of SWCNT-B, bordering on the remote ones, make $ring_2$.

Using the developed program SeamMaker, the construction of junctions between SWCNTs was carried out. Since when constructing a single junction, randomization is performed at each stage of the algorithm, the resulting models may have topological differences. In rare cases, during the operation of the algorithm, the construction procedure does not converge when each of the possible variants does not lead to a satisfactory configuration. In this case, the algorithm is interrupted when the maximum number of iterations is reached and the process starts again. This restriction is not fundamental, since restarting and, in some cases, a slight modification of the intermediate configuration solves this problem. In general, it is not possible to get around this limitation.

The construction of one junction of SWCNTs can take from 30 to 200 cycles of the main algorithm for SWCNTs of the considered diameter. Examples of the constructed T- and X-shaped junctions are shown in Fig. 6. T-shaped junctions between SWCNTs will be denoted as $T[n_1, m_1/n_2, m_2]$, where (n_1, m_1) — chirality of the first SWCNT, (n_2, m_2) — chirality of the second SWCNT and the end of the second SWCNT joins the first SWCNT. Similarly, X-shaped junctions will be denoted as: $X[n_1, m_1/n_2, m_2]$.
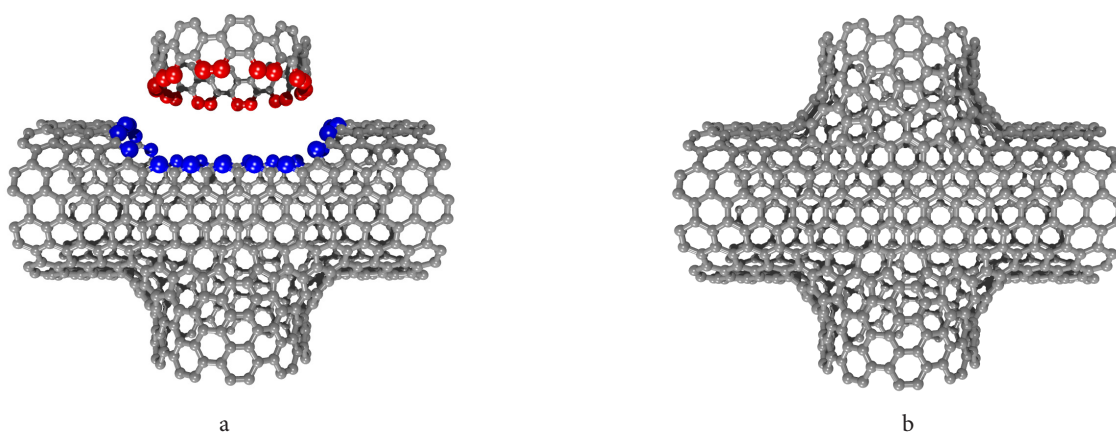

Fig. 5. (Color online) Construction of an X-shaped junction between two SWCNTs with chirality (10,10): preparatory phase for the creating the building of T-junction (a), building an X-shaped junction between two SWCNTs (10,10) (b).
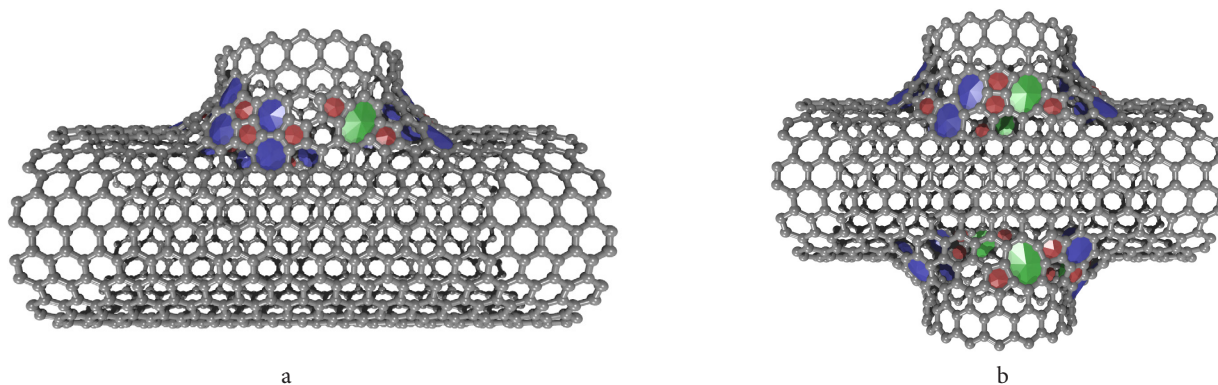

Fig. 6. (Color online) Junction models obtained using SeamMaker: T [13,13/21,0] (a), X [11,11/18,0] (b). Red color indicates pentagons, blue color — heptagons, green color — octagons.

4. Conclusions

The algorithm proposed in this paper allows the automatic construction of a large sample of full-atomic models of junctions between SWCNTs. The algorithm was implemented using Python and C++. Models constructed using the proposed algorithm can be used to theoretically study the effect of the topology of complex carbon structures on their mechanical properties and electrical conductivity. The practical significance of this algorithm is related to the possibility of calculating the statistically averaged physical characteristics of materials containing a large number of seamless junctions between SWCNTs. It should be noted that the approach used in the development of the algorithm can be generalized to construct full-atomic models of other structures containing carbon surfaces of complex shape, for example, graphene nanoblisters, fullerenes, glassy carbon, etc.

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