Simulation of the processes of carbon atom and nanographene interaction with a molecule of fullerene C$_{60}$

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Abstract. The results of numerical simulation of the processes of adsorption of a fullerene molecule by the nanographene edge is presented. It has been found that, as a result of adsorption, the spherical symmetry of the C$_{60}$ fullerene molecule is broken and this symmetry violation depends on a method of adsorption on the graphene surface. The results of numerical simulation of scattering of carbon atoms and dimers by a C$_{60}$ fullerene molecule have been also considered. The main goal is to determine the qualitative conditions for encapsulation of carbon atoms inside the fullerene molecule. It has been found that the predominant processes are scattering and adsorption of scattered carbon atoms with a minimal quantity of encapsulated atoms.

1. Introduction
Fullerenes are an independent allotropic form of carbon in the form of isolated molecules self-organized as convex closed polyhedra composed of the even number of three-coordinated carbon atoms. Defect-free fullerenes consist of geometrically regular hexagons (see Fig. 1a) and geometrically regular pentagons (see Fig. 1b) while the defect-free graphene consists of hexagons only (see Fig. 1c).

Figure 1. a) hexagon, b) pentagon highlighted by black circles for the example of the atomic structure of the fullerene C$_{60}$, c) atomic structure of defect-free 112-atomic rectangular portion of graphene (only hexagons with periodicity of boundary conditions).

Among fullerenes, the fullerene C$_{60}$ is most symmetrical and stable. It is formed by 20 hexagons and 12 pentagons; at their tops are carbon atoms. Another structural feature of the fullerene is that it has an inner cavity of approximately 5 Å in diameter where the atoms of other elements or even small molecules can be located. The fullerene properties can differ if it is combined with other atoms and molecules. Endohedral fullerenes are of particular interest when additional atoms, for example alkali metal ones, are inside the fullerene. However, the practical application of fullerenes in nanoengineering raises the question on which substrate the fullerene structures will be. Such substrates can be the crystal surface of silicon carbide, silicon, diamond and graphene; the latter is more...
successful in terms of miniaturization since its thickness is only one atomic layer. In addition, defect-free graphene being a two-dimensional hexagonal crystalline lattice of carbon is a structure with distinctive physical properties.

In the present work, the adsorption of fullerene $C_{60}$ on the surface of defect-free graphene and its edges is considered by the methods of computer simulation in the framework of classical molecular dynamics. The processes of scattering of carbon atoms and dimers by fullerene are also considered to establish the conditions for encapsulation of scattered atoms inside fullerenes.

2. Modeling and simulation method

2.1. Computer simulation of the interaction of defect-free single fullerene $C_{60}$ and nanographene

At first, a computer model of a single defect-free fullerene $C_{60}$ was constructed by the energy minimization method with the second-generation Brenner potential (REBO) that well describes carbon structures [1] (the coordinates of carbon atoms were taken from [2]). Then a computer model of “infinite” defect-free graphene was constructed; this model is intended for consideration of fullerene adsorption on the graphene surface. For this, a rectangular graphene region consisting of 112 carbon atoms was chosen (Fig. 7; see details and justification of such a model in [3]). Then, by the same method of energy minimization with the Brenner potential and with the periodic conditions imposed on the boundary atoms, a computer model of infinite defect-free graphene with the distance between nearest atoms of 1.4 Å and the cohesion energy $E_c$ of 7.4 eV for each atom was obtained.

For the fullerene adsorption on the graphene edges to be considered, a computer model of defect-free nanographene was built. For construction of this model, the same sequence of actions was used as for construction of the model of “infinite” defect-free graphene but with no periodic conditions imposed on the boundary atoms. As a result, nanographene was obtained with the distance between its nearest atoms of approximately 1.4 Å (see Fig. 2). The cohesion energy of 82 inner atoms (i.e. the atoms having chemical bonds with three neighboring atoms) is 7.4 eV, and only for 2 inner atoms this energy is 7.8 eV; the energy values for the remaining atoms are shown in Fig. 2.

2.2. Simulation of the processes of scattering of carbon atoms and dimers by fullerene

To simulate the scattering of carbon atoms and dimers, a computer model consisting of 100 fullerene molecules and scattered atoms (dimers) was built (Fig. 3). The scattering of atoms and dimers was perpendicular to the YZ plane in accordance with the coordinates of the fullerene atoms given in [2]. The size of the scattering region was determined by the size of the fullerene molecule. The aiming points at which the carbon atoms (dimers) were scattered were determined by a “grid” with a step of 0.2 Å overlapped on the scattering region. The energy range of scattered atoms (dimers) was mainly...
determined by [4]. For scattering of carbon dimers, two cases were realized: the dimer axis was oriented along the scattering direction and perpendicular to it.

![Figure 3.100 molecules of fullerene with scattered carbon atoms (dimers) by them.](image)

3. Results and discussion

3.1 Computer simulation of fullerene adsorption on graphene

After the computer models of single defect-free fullerene $C_{60}$, “infinite” graphene and nanographene were obtained, the fullerene adsorption was studied first on graphene and then on its edges. To study the adsorption of fullerene on graphene, the computer models of fullerene and “infinite” graphene were approached to the required distance with a different set of geometric arrangement of fullerene relative to the graphene surface and after that the energy minimization method within the framework of the Brenner potential and periodic boundary conditions on the edge graphene atoms was applied.

It was found that the adsorption of fullerene $C_{60}$ on the graphene surface can be realized in different ways; only 5 selected methods of such adsorption are listed here with indication of the method name in parentheses according to [5], if any:

(i) the interaction of one fullerene atom and one graphene atom (C-ATP),
(ii) the interaction of fullerene hexagons and graphene (C-RING),
(iii) the interaction of two neighboring fullerene atoms and two neighboring graphene atoms (BRI),
(iv) the interaction when the fullerene hexagon center is located over the graphene atom (C-RING2),
(v) the interaction of two nearest non-adjacent atoms of fullerene and two nearest non-adjacent atoms of graphene.

| Adsorption method | Calculation method | Experiment [7] |
|-------------------|--------------------|----------------|
| I, C-ATP          | Brenner potential | 0.85           |
| II, C-RING        | PBE                | 1.08           |
| III, BRI          | PBE-D2             | 0.77           |
| IV, C-RING2       | ptB86b             | 1.07           |
| V                 |                     | 0.06           |
|                   | PBE                | 0.84           |
|                   | PBE-D2             |                |
|                   | ptB86b             |                |

| Adsorption method | Calculation method | Experiment [7] |
|-------------------|--------------------|----------------|
| I, C-ATP          |                    | 2.62           |
| II, C-RING        |                    | 2.69           |
| III, BRI          |                    | 2.69           |
| IV, C-RING2       |                    | 2.19           |
| V                 |                    | 2.22           |

Table 1. Comparison of the obtained results (shown in bold) with the first-principle calculations and experimental data on the binding energy (eV) of fullerene with nanographene.
As it turned out, as a result of adsorption, the spherical symmetry of fullerene \( \text{C}_{60} \) is broken and this violation of symmetry depends on a method of adsorption on the graphene surface. The binding energy and the distance of adsorption for adsorbed fullerene \( \text{C}_{60} \) were obtained; they were compared with the available experimental and theoretical data (see Table 1). It was experimentally obtained in [6] that the binding energy of fullerene \( \text{C}_{60} \) with graphene is 0.85 eV and the shortest distance between atoms of fullerene \( \text{C}_{60} \) and graphene is 2.9 Å; this value can be considered as experimentally measured distance of adsorption. In [5] by three \textit{ab initio} methods: PBE, PBE-D2 and optB86b the binding energy and adsorption distance were obtained for the adsorption ways from I to IV; no geometric changes in adsorbed fullerene \( \text{C}_{60} \) are found in this work.

Three variants of fullerene adsorption on the nanographene edges were considered (see Fig. 4): 1) in the middle of the zigzag edge of nanographene, 2) in the middle of armchair edge and 3) at the utmost “angular” atom of nanographene.

![Figure 4: Visual representation of the interaction of adsorbed fullerene \( \text{C}_{60} \)](image)

In all of these variants of adsorption, the geometric center of fullerene was initially set in the plane in which nanographene is located. After the appropriate initial relative position of defect-free fullerene and nanographene was set the binding energies of adsorbed fullerene with nanographene were found by the method of energy minimization. From the data obtained, it was found that fullerene is adsorbed best on the armchair edge of nanographene, worst of all on the “angular” atom of nanographene. For adsorption to the nanographene edge the binding energy can be almost two times higher than the highest binding energy for adsorption on the graphene surface. In this case the great deformation of fullerene is observed.

### 3.2 Simulation of the processes of scattering of carbon atoms and dimers by fullerene

For simulation of the scattering processes of carbon atoms (dimers) by fullerene molecules, we varied the energy of the incident particles within the range 10-30 eV. Within the energy range 10-15 eV/atom, the adsorption of incident atoms was observed; partial destruction of the fullerene shells was observed for energies 20-25 eV/atom. No encapsulation of carbon atoms occur. With a further increase in the energy of the incident carbon atoms, partial or complete destruction of the fullerene shell takes place though, but in this case there is no encapsulation of the incident atoms as well.

For the quantitative estimation of the processes of scattering, adsorption, and carbon atom encapsulation by the fullerene molecule, the following model experiment was conducted for the scattering of carbon atoms with the energy of 25 eV and different aiming parameters in the YZ direction to fullerene. The projection of fullerene atoms onto the YZ plane is symmetric, so the scattering was carried out only in the region of the first quarter (Fig. 5a). In this quarter, 400 atoms were scattered. For clarity (using the target symmetry), the result is mirrored for the other quarters (Fig. 5b). The choice of energy was determined by the fact that for its lower values the pronounced adsorption or inelastic scattering (penetration) of incident carbon atoms was observed. Of the 400 atoms, only one atom was encapsulated. With an increase in energy up to 30 eV, there is no encapsulation.
Considering the comparability of carbon-carbon binding energy as a determining factor of the absence of encapsulated atoms and the pronounced adsorption of incident atoms, we carried out the following model experiment. We scattered the dimers of carbon atoms by fullerenes whose axis is oriented along the direction of dimer motion. The number of endohedral fullerenes, at best, reached 5-7 fullerenes with encapsulated atoms per hundred fullerenes (while maintaining the integrity of fullerenes, Fig. 6). As shown by model experiments, in the scattering of carbon dimers, the dimer orientation has a significant effect on the number of endohedral fullerenes. The largest number of endohedral fullerenes was obtained when the axis was oriented along the scattering direction (up to ten endohedral fullerenes per hundred fullerenes). However, upon reaching the largest possible number of endohedral fullerenes, the number of fullerenes damaged and destroyed as a result of this process increases significantly. When the dimer axis is oriented perpendicular to the direction of motion, the results do not qualitatively differ from those obtained by scattering of single atoms.

4. Conclusion
Fullerene adsorption on graphene has a wide variety defined both by a different quantity of fullerene atoms through which chemical bonds with graphene atoms are established and by geometric arrangement of adsorbed fullerene, for example, the ability to be adsorbed on the graphene edges. Defects of fullerene and graphene, as well as endoatoms, can play some role in the adsorption under consideration. The found values of the binding energy of fullerene with graphene, some of which were compared with published theoretical and experimental results, also have a significant range from 0.06 to 2.60 eV.
The above described model experiments for the scattering of carbon atoms and dimers by fullerenes have shown that the formation of endohedral fullerenes by scattering of particle beams by them, apparently, cannot be considered quite effective. Both the destruction of the fullerene skeleton and the adsorption of scattered atoms are observed. The predominant processes are scattering (for energy above 20 eV) and adsorption (for energy of about 10 eV).

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