Computer simulation of the interaction of ringlike carbon clusters with nanographene

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Abstract. Various cases of interaction of ringlike carbon clusters $C_7$, $C_{12}$ and $C_{13}$ with a rectangular nanographene consisting of 272 atoms were studied and presented. It was found that this interaction results in the structural change in these clusters and in the local part of nanographene. The cohesive energies of these clusters in the isolated (free) state and their binding energies with nanographene have been calculated. The results show that despite this interaction the atoms of cluster are hold together as a single cluster thanks to the significantly higher cohesive energy of cluster the its binding energy with nanographene.

1. Introduction

Graphene term was originally used to refer to an abstract model, namely, a single layer of graphite atoms which do not interact with other objects. Even at those theoretical studies, it was clear that graphene, whether in reality, would have the number of unique properties, such as high electrical and thermal conductivity. In 2004 A. Geim with his coworkers [1] received a single sheet of graphene experimentally in the laboratory, thus the term graphene has become point not only to an abstract model, but also on the nature of the real object. As the real object of nature graphene interacts with the environment and in particular with atoms, molecules and their ensembles as clusters.

There are a large number of works dealing with the interaction of graphene with atoms and molecules. Using different methods, this interaction was studied in different aspects. Nevertheless, the very first question is that you need to decide how mathematically infinite graphene according to its ideal model can be constructed to result in an object suitable for computer simulation. For this aim two approaches are usually used: periodic boundary conditions are imposed on the final size of the graphene and thus it is defined as an infinite, or piece of graphene is taken. We use the later approach in our studies as in practice the graphene with finite size called as nanoribbons are commonly used.

With regard to research methods, either the classical molecular dynamics method with the corresponding interatomic potentials, e.g. Brenner potential [2], Tersoff potential [3], Universal force field [4] or ab-inito methods (Metod of Hartree-Fock-Roothaan, Moller–Plesset perturbation theory, theory of the combined clusters and so on) are mostly used.

The choice of methods ab-inito is inevitable if you need to determine the parameters that cannot be defined using classical molecular dynamics, for example, spin, magnetic moment, etc. However, if you focus on the configuration and the cohesive energy of the atoms, the Monte Carlo and the classical molecular dynamics methods are more suitable than the ab-inito methods as later ones require significantly long time for calculation and some specific parameters. We note that the ultimate goal of studies of the interaction of atoms and molecules with graphene can be different. In particular, the graphene can be bent or rolled in a tube as a result of this interaction (for example, by deposition of particles along a single line) [5]. In other case, the local change of graphene, including the question of transition of graphene in graphane was studied when a hydrogen atom interact with it [6]. As for the atoms, which interact with graphene, the H, F, O and C atoms, metal atoms and the molecules of organic substances are more often chosen.
Our work focuses on the change in the shape of $C_7$, $C_{12}$ and $C_{13}$ clusters by interacting them with nanographene and on binding energy of clusters with nanographene.

2. Modeling and simulation method

The method of energy minimization is a common technique to calculate the equilibrium configuration of molecules and clusters. The basic idea of this method is that a stable state of a molecular system corresponds to a local minimum of the potential energy [7]. The state with the lowest energy corresponds to the ground state, while other local minima are metastable states. In this paper, we use the so-called Brenner second-generation reactive empirical bond order (REBO) potential [2], which is specifically parameterized for the carbon and hydrogen-carbon systems. In [6, 8] it was shown how well REBO potential describes some characteristics of carbon clusters, graphene, and graphane.

As ringlike carbon clusters are the most stable among the other small carbon clusters of different configurations with the same number of atoms [8], we use ringlike conformation of $C_7$, $C_{12}$ and $C_{13}$ clusters. Their stable structures were found using the energy minimization method. The radii of these clusters and the cohesive energy $E_{\text{coh}}$ of their atoms are shown in Table 1.

| Cluster | Radius (Å) | $E_{\text{coh}}$ (eV/atom) |
|---------|------------|-----------------------------|
| $C_7$   | 1.58       | 5.51                        |
| $C_{12}$| 2.59       | 5.90                        |
| $C_{13}$| 2.80       | 5.93                        |

The stable state of graphene which hereinafter called nanographene with a rectangular shape of $32.7 \times 19.9$ Å consisting of 272 atoms was found by the method of energy minimization. We note that the internal atoms of nanographene have cohesive energy $E_{\text{coh}}=7.39$ eV/atom, whereas its boundary atoms, the total number of which is 48, have cohesive energy $E_{\text{coh}}=4.9\div5.2$ eV/atom. The free 272-atomic rectangular nanographene and ringlike $C_7$, $C_{12}$ and $C_{13}$ clusters are presented in Fig. 1.

Figure 1. (Color online) Stable configurations of 272 atomic nanographene (a) and ringlike carbon clusters: $C_7$ (b), $C_{12}$ (c) and $C_{13}$ (d).
After creating of nanographene and C\(_7\), C\(_{12}\) and C\(_{13}\) clusters their possible interactions with each other were studied. Initial position of C\(_7\), C\(_{12}\) and C\(_{13}\) cluster was at an angle to the nanographene \(\alpha = 0^\circ, 15^\circ, 30^\circ, 45^\circ, 60^\circ, 75^\circ \text{ and } 90^\circ\), where \(\alpha\) is the angle between the normal of nanographene and the cluster plane. The initial height of ringlike clusters, which is defined as the smallest distance from the atom of cluster to the plane of nanographene, was \(h_7 = 0.127\text{Å}, h_{12} = 0.149\text{Å}\) and \(h_{13} = 0.101\text{Å}\). Here \(h_7\), \(h_{12}\) and \(h_{13}\) are heights of ringlike C\(_7\), C\(_{12}\) and C\(_{13}\) clusters, respectively. To avoid or minimize the edge effects the center of nanographene was chosen as the place of interaction with the ringlike clusters.

3. Results and discussion

The cluster interaction with nanographene takes place by a way of forming bonds between some atoms of the cluster and nanographene. In Fig. 2 we present the results of our computer simulation for the final positions of cluster-nanographene system when the ringlike clusters interact with nanographene forming bonds with their one or two atoms. These bonds define the cohesion energy of the cluster with nanographene. If one atom of the cluster forms a bond with nanographene as shown in Fig. 2 (a), then the binding energy of this atom with graphene very well estimates the cohesion energy of the whole cluster with nanographene. When several atoms of the cluster have bonds with graphene atoms, we define the maximal value of the binding energy of the cluster atom with nanographene and the sum of all the binding energies of the cluster atoms with the nanographene atoms, which makes it possible to estimate the total cohesion energy of the whole cluster with nanographene.

![Figure 2. (Color online) Interaction of C\(_7\), C\(_{12}\) and C\(_{13}\) clusters through their one or two atoms. Red spheres are nanographene atoms, blue spheres are cluster atoms and green ones are cluster atoms that interact directly with nanographene. a - C\(_{12}\) and \(\alpha=30^\circ\), b - C\(_7\) and \(\alpha=0^\circ\), c - C\(_7\) and \(\alpha=60^\circ\), d - C\(_7\) and \(\alpha=75^\circ\), e - C\(_{12}\) and \(\alpha=0^\circ\) or \(\alpha=75^\circ\), f - C\(_{13}\) and \(\alpha=0^\circ\), g - C\(_{13}\) and \(\alpha=30^\circ\), h - C\(_{13}\) and \(\alpha=45^\circ\), where \(\alpha\) indicates an initial position of cluster.](image)

The interaction of carbon clusters with nanographene causes the changes both in the electronic structure and in geometric shape of graphene and cluster. The carbon cluster changes the hybridization from \(sp^2\) to \(sp^3\) for the graphene atoms bonded with cluster. This change of hybridization causes a local structural change in the graphene sheet: the graphene atoms bonded with cluster are shifted above the plane of graphene (see Fig. 2). Some atoms of cluster also can be displaced out of the cluster plane due to its interaction with nanographene (see, e.g. Fig. 2 d, e).
In Fig. 3 the final stable states of cluster-nanographene system, when the ringlike clusters interact with nanographene forming bonds through their more than two atoms, are presented. As seen, the interaction results in significant buckling the shape of clusters in these cases. The several possible cases of such interaction are observed. In particular, the ringlike cluster can interact with nanographene through its some part as shown in Fig. 3 (a, b, d-f), keeping its other part quite far from the nanographene plane. Another typical case of interaction is that when the cluster interacts through its atoms which are not neighbor each other. In this case, though cluster interacts through its few atoms, all its atoms are not far from graphene (see, Fig. 3, g-i).

Figure 3. (Color online) Interaction of C\textsubscript{7}, C\textsubscript{12} and C\textsubscript{13} clusters through its more than two atoms. Red spheres are nanographene atoms, blue spheres are cluster atoms and green ones are cluster atoms that interact directly with nanographene. a – C\textsubscript{7} and $\alpha$=15\textdegree, b - C\textsubscript{7} and $\alpha$=30\textdegree, c - C\textsubscript{12} and $\alpha$=15\textdegree, d - C\textsubscript{12} and $\alpha$=45\textdegree, e - C\textsubscript{13} and $\alpha$=15\textdegree, f - C\textsubscript{13} and $\alpha$=60\textdegree, g - C\textsubscript{7} and $\alpha$=90\textdegree, h - C\textsubscript{12} and $\alpha$=90\textdegree, i - C\textsubscript{13} and $\alpha$=90\textdegree. Underlined g, h and i correspond to the top view of g, h and i images.

These results show that the different possible cases of the interaction increase with increasing the number of atoms in cluster. Note that in some cases the cluster can cause the vacancy of atoms in nanographene breaking the bonds of a few atoms of nanographene. If an initial position of cluster results in breaking the several bonds and formation of new structure near to the nanographene which are forbidden, this case can cause the failure of interaction. Therefore, there are some initial angles $\alpha$, in which the computer simulation does not determine the final configuration of the atoms, i.e. these positions cause a failure of interaction. These unsuccessful angles for C\textsubscript{7}, C\textsubscript{12} and C\textsubscript{13} clusters in the studied case are $\alpha$=45\textdegree, 60\textdegree and 75\textdegree, respectively. However, note that these values can be depended on the place of interaction, azimuthal angle of cluster position, etc.
In Table 2 we summarize the cohesion data of the C\textsubscript{7}, C\textsubscript{12} and C\textsubscript{13} clusters interacting with nanographene versus the initial angle \(\alpha\) of cluster position. Analyzing the results on the images of interaction and the cohesion data of clusters, we found that the maximal binding energy corresponds to the final upstanding position of clusters (i.e. when the planes of cluster and nanographene become perpendicular). As seen from Table 2, the maximal binding energy is 1.38, 1.59 and 2.93 eV for the C\textsubscript{7}, C\textsubscript{12} and C\textsubscript{13} clusters interacting with nanographene, respectively. These values are considerably smaller than the cohesive energy \(E_{\text{coh}}\) of clusters presented in Table 1. That is why we can conclude that the atoms of clusters are hold together as a single cluster despite their interaction with nanographene. The cluster can be desorbed as a single cluster easily by e.g. heating the nanographene.

In the studied cases the highest value of the sum of binding energy is 4.66 eV for the C\textsubscript{7} cluster, 3.82 eV for the C\textsubscript{12} and 5.89 eV for the C\textsubscript{13} cluster with 4, 5 and 6 bonded atoms, respectively (Table 2). These configurations form the strongest bond between the ringlike cluster and nanographene.

It should be noted that in the most cases the cluster or its main part hold a ringlike structure during its interaction with nanographene. However, in the case of its lying position, the cluster is more buckled by its atoms bonded with nanographene (see, e.g. Fig. 2 d and Fig. 3 c, h, i). The interaction in the case of large clusters can result also in the change of the ringlike shape shown as in Fig. 3, i: the top view of the C\textsubscript{13} cluster became more triangular shape.

### Table 2. The cohesion data of the C\textsubscript{7}, C\textsubscript{12} and C\textsubscript{13} clusters interacting with nanographene.

| Cluster | Initial angle \(\alpha\) (degrees) | The maximal binding energy (eV) | The sum of binding energy (eV) | The number of atoms interacting with nanographene |
|---------|-------------------------------------|---------------------------------|-------------------------------|----------------------------------------|
| C\textsubscript{7} | 0                                  | 0.78                            | 1.41                          | 2                                      |
| C\textsubscript{7} | 15                                 | 0.93                            | 3.21                          | 4                                      |
| C\textsubscript{7} | 30                                 | 1.37                            | 4.66                          | 4                                      |
| C\textsubscript{7} | 60                                 | 1.37                            | 2.52                          | 2                                      |
| C\textsubscript{7} | 75                                 | 1.38                            | 2.12                          | 2                                      |
| C\textsubscript{7} | 90                                 | 1.35                            | 4.22                          | 4                                      |
| C\textsubscript{12} | 0                                  | 1.51                            | 2.32                          | 2                                      |
| C\textsubscript{12} | 15                                 | 1.49                            | 3.14                          | 3                                      |
| C\textsubscript{12} | 30                                 | 1.59                            | 1.59                          | 1                                      |
| C\textsubscript{12} | 45                                 | 0.84                            | 3.82                          | 5                                      |
| C\textsubscript{12} | 75                                 | 1.51                            | 2.34                          | 2                                      |
| C\textsubscript{13} | 90                                 | 1.49                            | 3.35                          | 3                                      |
| C\textsubscript{13} | 0                                  | 0.57                            | 1.10                          | 2                                      |
| C\textsubscript{13} | 15                                 | 1.27                            | 5.45                          | 4                                      |
| C\textsubscript{13} | 30                                 | 2.93                            | 4.29                          | 2                                      |
| C\textsubscript{13} | 45                                 | 1.76                            | 3.16                          | 2                                      |
| C\textsubscript{13} | 60                                 | 1.11                            | 2.65                          | 4                                      |
| C\textsubscript{13} | 90                                 | 2.02                            | 5.89                          | 6                                      |

These results show that the interaction of carbon clusters with nanographene results in the deformation of both clusters and local part of graphene. As this interaction changes the hybridization from \(sp^2\) to \(sp^3\) for the graphene atoms bonded with cluster it can cause the local change of graphene properties, in particular its transition from the semimetal to the semiconductor.
3. Conclusion
Using an energy minimization method with a modified Brenner potential the stable structures of ringlike $C_7$, $C_{12}$ and $C_{13}$ clusters interacting with nanographene have been studied. Several possible configurations of these clusters were found. The cohesive energies of these clusters in the isolated (free) state and their binding energies with nanographene have been calculated. We found that these ringlike clusters can interact by one, two or more of its atoms with nanographene. It was shown that this interaction causes the structural change in both cluster and local part of graphene. As this interaction changes the hybridization from $sp^2$ to $sp^3$ for the graphene atoms bonded with cluster, the experimental investigation of this transition might be useful for the manipulation of the local changes of graphene properties.

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