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Reconstruction of carbon atoms around a point defect of a graphene: a hybrid quantum/classical molecular-dynamics simulation

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Abstract

We have investigated the rearrangement of carbon atoms around a point defect of a graphene using a hybrid *ab initio*/classical molecular-dynamics (MD) simulation method, in which 36 carbon atoms surrounding a point defect are treated by the *ab initio* MD method and the other 475 carbon atoms relatively far from the point defect are treated by the classical MD method. We have confirmed a formation of a 5-1DB defect (a pentagon and a dangling bond) from the time dependence of atomic configurations and electron density distributions obtained by our simulation. We have found that the pentagon is formed in two different positions around the point defect, and that the two positions appear alternately during the simulation, the frequency of which increases with increasing temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently we [1] have studied the thermal instability or 'melting' of *perfect* carbon nanotubes on the basis of classical molecular-dynamics (MD) simulations using an environment-dependent interaction potential (EDIP) [2] and found that the 'melting temperature' decreases with a decreasing radius of carbon nanotube. In actual carbon nanotubes, however, there exist various kinds of defects which may influence the electrical, thermal and mechanical properties of carbon nanotubes. Therefore it is important to investigate the effects of defects on thermal stability of carbon nanotubes.

So far there have been many studies on the effects of defects of carbon nanotubes on their various physical properties. For example, Ajayan *et al* [3] investigated the surface reconstruction of single-walled carbon nanotubes by the electron irradiation experiment and by the tight-binding MD simulation, and found that the surface reconstruction and size reduction occur through dangling bond saturation and defects forming with nonhexagonal rings such as a 5-1DB defect(a pentagon and a dangling bond). Lu and Pan [4] investigated the nature of a single vacancy in carbon nanotubes based on the tight-binding method and the steepest-descent algorithm and found that effects of the point defect on the structure of carbon nanotubes depend on the radius and chirality as well as the electric properties, and that the 5-1DB defect is formed without any constraint.

The purpose of this paper is to investigate the rearrangement of atoms around a point defect (vacancy) of a graphene. The graphene is an interesting system in itself and also can be considered as a limit of a carbon nanotube with infinite radius. Though carbon atoms of the graphene are connected with each other by three-fold sp^2-bonds, each of the three nearest-neighbour carbon atoms of the vacancy has a

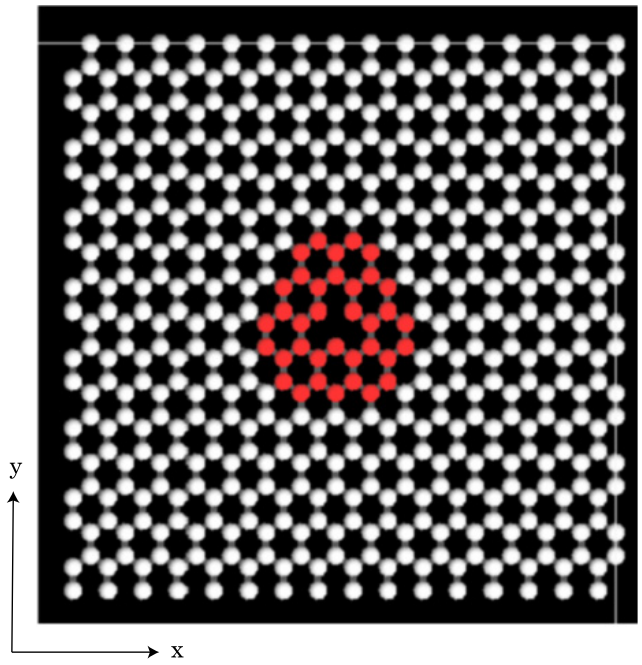

Figure 1. A model graphene system with a single vacancy at the centre. The 36 carbon atoms in the cluster region are shown by grey (red in the colour version) balls and the 475 carbon atoms in the surrounding environmental region are shown by white balls.

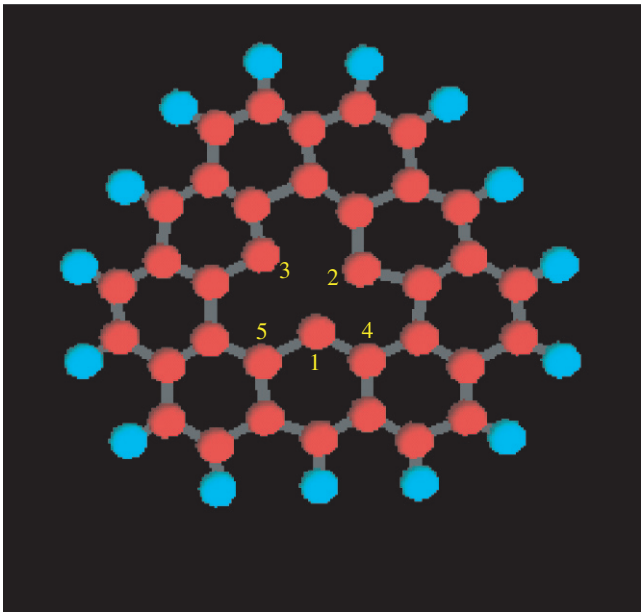

Figure 2. The atomic configuration of the cluster region composed of 36 carbon atoms (red) and a single vacancy at the centre. The carbon atoms labelled from nos 1 to 3 are nearest-neighbour atoms of the vacancy and have dangling bonds, while the carbon atoms nos 4 and 5 are the next-nearest-neighbour carbon atoms. We also show the terminator 15 hydrogen atoms (blue) to terminate those dangling bonds in the *ab initio* MD simulations.

dangling bond. Therefore, we have to treat the carbon atoms around the vacancy quantum mechanically to investigate the rearrangement of atomic configuration based on the bonding states. For this purpose we have employed a hybrid *ab initio*/classical MD simulation method to investigate the time dependence of atomic configurations and electron density distributions.

2. Method of calculation

2.1. A hybrid ab initio/classical MD simulation

We use the hybrid *ab initio*/classical MD simulation [5–7], in which a system (referred to as S in the following) is divided into a cluster region (referred to as C) and an environmental region. The atoms in the cluster region are treated by *ab initio* MD simulations based on the density-functional theory (DFT), while the atoms in the environmental region are treated by classical MD simulations using EDIP [2].

The potential energy of the total system is defined as follows,

$$E(\boldsymbol{r}_i \in \mathrm{S}) = E_{\mathrm{classical}}(\boldsymbol{r}_i \in \mathrm{S}) - E_{\mathrm{classical}}(\boldsymbol{r}_i \in \mathrm{C}) + E_{ab\ initio}(\boldsymbol{r}_i \in \mathrm{C}), \quad (1)$$

where $\boldsymbol{r}_i$ is the coordinates of the ith atom, $E_{ab\ initio}$ is the potential energy obtained by the *ab initio* calculation based on the DFT and $E_{\mathrm{classical}}$ is the potential energy calculated using EDIP. The potential energy of cluster atoms needs to be calculated by both DFT and EDIP calculations. We choose the cluster region in such a way that at least two covalent bonds for each carbon atom are included in the cluster. Since there is a dangling bond per each outermost carbon atom of the cluster, we terminate these dangling bonds. In the *ab initio* calculation, hydrogen atoms are introduced to terminate the dangling bonds of the cluster and their coordinates are given as a function of atomic coordinates in both the cluster and the environmental regions.

Our *ab initio* MD simulation is based on the DFT, where the generalized gradient approximation (GGA) [8] is used for the exchange–correlation energy. The electronic wavefunctions and the charge density are expanded in plane waves with cutoff energies 20 and 180 Ryd, respectively. As for the Brillouin zone sampling, we use Γ-point sampling. The energy functional is minimized using an iterative scheme based on the preconditioned conjugate-gradient method [9, 10]. The ultrasoft pseudopotential is used for interaction between valence electrons and ions [11].

In the classical MD simulation, we use the environment-dependent interaction potential (EDIP) proposed by Marks [2]. EDIP is represented as a sum of the pair potential and the three-body potential, which are the function of not only the distance between two atoms and the angle formed by three atoms for three-body potential, but also the generalized coordination number of the atoms. The potential energy calculated by the EDIP depends on the local environment of the atoms through this generalized coordination number. The validity of the EDIP has been checked for liquid and amorphous carbons [2, 6] by *ab initio* MD simulations, suggesting a very good transferability of the EDIP.

We have also confirmed the validity of our hybrid *ab initio*/classical MD method using EDIP by applying the hybrid method to the graphene for investigating the dynamic properties such as the heat transfer [6] and also

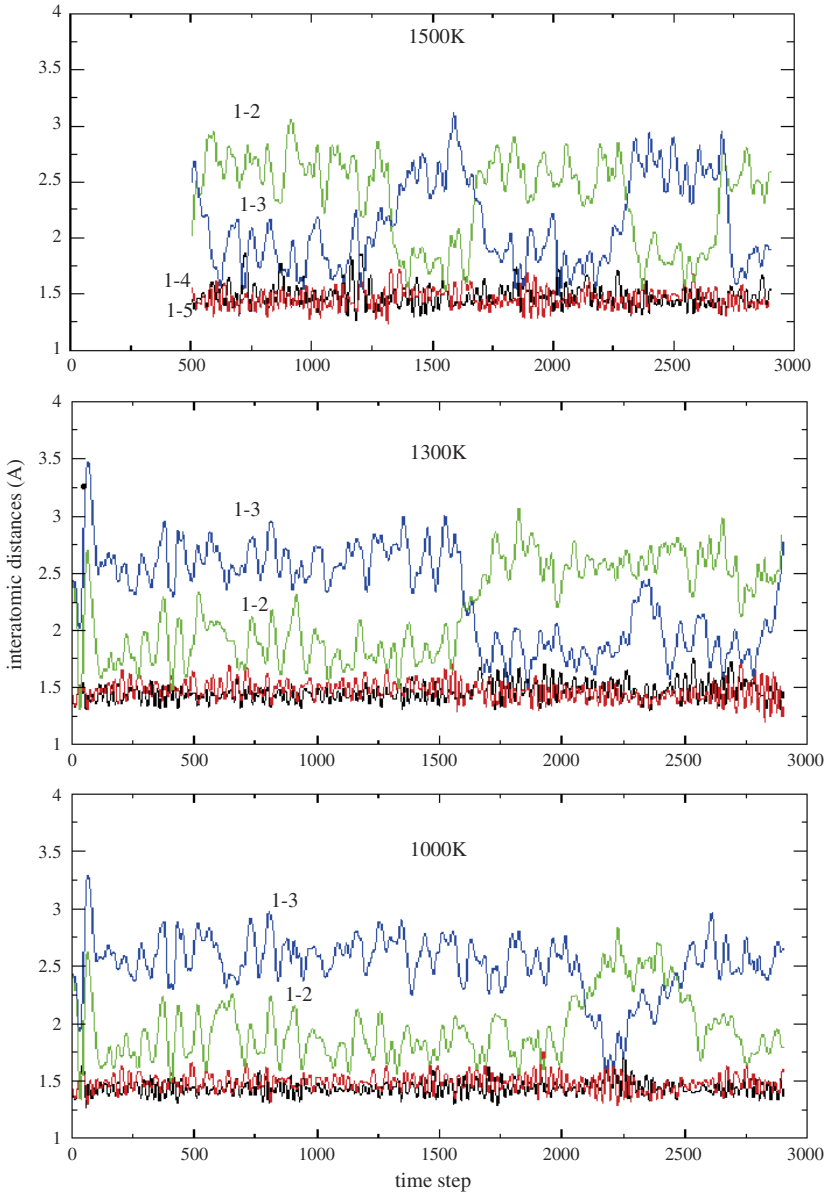

Figure 3. The time-step dependences of the interatomic distances between carbon atoms 1–2 (green), 1–3 (blue), 1–4 (red) and 1–5 (black) shown in figure 2.

to the hydrogenated nanostructured graphite for studying the desorption of hydrogen atoms [7].

2.2. Details of calculation

Our model system is a graphene sheet with a single vacancy at the centre as shown in figure 1. The nearest-neighbour distance between carbon atoms is taken to be 0.142 nm, which is the bond length of graphite. The 36 carbon atoms (grey (red in the colour version) balls in figure 1) surrounding a point defect in the cluster region are treated by an *ab initio* MD method and the other 475 carbon atoms (white balls) in the environmental region relatively far from the point defect are treated by a classical MD method. We apply the periodic boundary condition in the x direction in figure 1.

We have carried out MD simulations for the model graphene shown in figure 1. At each temperature we carried out MD simulations for 3500 steps with a time-step $\Delta t = 0.6$ fs and calculated physical quantities using the last 3000 steps (the first 500 steps were used for thermal equilibration). We started our MD simulation for the initial configuration shown in figure 1 and then increased the temperature. We repeated this procedure at three temperatures of 1000, 1300 and 1500 K, and obtained the time dependence of the atomic configurations and electron density distributions.

3. Results and discussion

3.1. The time dependence of the atomic configuration

In figure 2 we show the initial atomic configuration for the cluster calculation, which is composed of 36 carbon atoms (red) and a vacancy at the centre. The carbon atoms labelled 1–3, which are the nearest-neighbour atoms of the central vacancy, are two-fold coordinated and have dangling bonds;

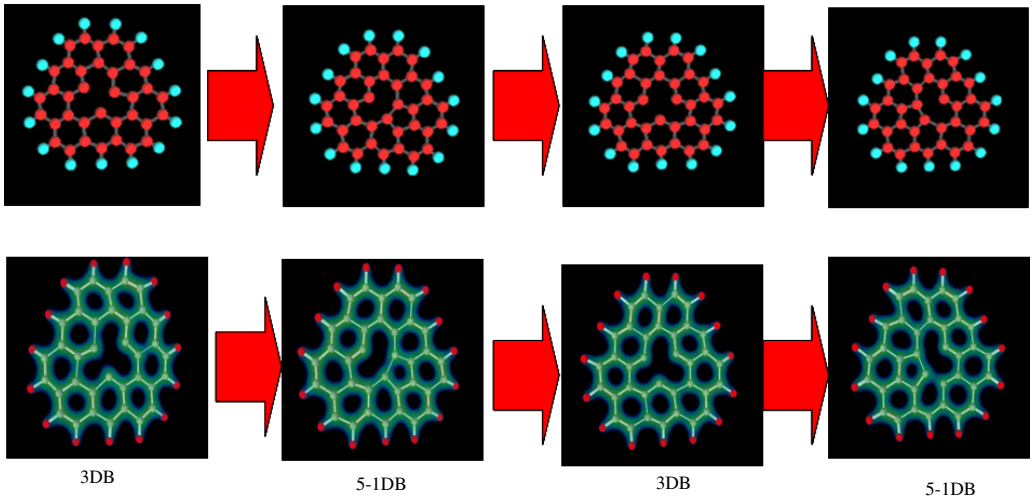

Figure 4. The time dependence of atomic configurations (upper) and electron density distributions (lower). The atomic configuration with three dangling bonds (3DB) and that with a pentagon and a dangling bond (5-1DB) appear alternately.

a dangling bond per each carbon atom. The carbon atoms labelled 4 and 5 are the next-nearest-neighbour atoms of the vacancy. The 15 hydrogen atoms (blue) are introduced in the *ab initio* MD simulation to terminate those dangling bonds of outermost carbon atoms of the cluster region.

In figure 3 we show the time-step dependence of the interatomic distances between carbon atoms labelled 1–2 (green), 1–3 (blue), 1–4 (red) and 1–5 (black) in figure 2 at three temperatures of 1000, 1300 and 1500 K. As is seen from figure 3, the interatomic distances between 1–2 (green) and 1–3 (blue) change significantly as a function of time steps and sometimes cross each other. With increasing temperature, alternation of the interatomic distances 1–2 and 1–3 curves occur more frequently. The interatomic distances between 1–4 (red) and 1–5 (black) remain almost unchanged, being about 0.142 nm = 1.42 Å, which is the bond length of the initial atomic configuration shown in figure 1.

3.2. Formation of a 5-1DB defect

In figure 4 we show the atomic configurations corresponding to the alternation of the interatomic distances 1–2 and 1–3 shown in figure 3. As is seen from figure 4, when the interatomic distance 1–2 is shorter, the pentagon of carbon atoms is formed at the lower right of the vacancy together with the nonagon at the upper left. Thus we have confirmed a formation of a 5-1DB defect. This is understood, since there are three dangling bonds (referred to as 3DB in figure 4) for an original point defect, i.e. for an initial atomic configuration, and there is a single dangling bond for a 5-1DB defect, and therefore the latter is favourable energetically. However, since the temperature of the system considered here is rather high, 1000–1500 K, the reconstructed atomic configuration, 5-1DB, is not stable due to the thermal motion of carbon atoms around the vacancy. We have found that the pentagon is formed in two different positions, at the lower right and lower left of the vacancy, and that the two positions appear alternately during the simulation, the frequency of which increases with increasing temperature.

4. Conclusion

We have applied the hybrid *ab initio*/classical MD simulations to the model system for a graphene with a single vacancy to investigate the atomic rearrangement around the vacancy. We have found from the time dependence of the atomic configuration and the electron density distribution obtained from our simulation that (i) a 5-1DB defect is formed, though it is not stable at high temperatures of 1000–1500 K, and that (ii) a pentagon is formed in two different positions, which appear alternately.

Acknowledgments

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