



# Molecular dynamics simulations of amorphous carbon structures

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## Abstract

The formations of different kinds of carbon structures have been studied by means of molecular dynamics simulations. A chain-like amorphous structure was obtained on diamond (111) surface with fivefold, sixfold, and sevenfold rings. At the temperature of 3500 K in the bulk region amorphous, graphite- and diamond-like structures were developed depending on the macroscopic density. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Carbon; Molecular dynamic simulation; Amorphous

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## 1. Introduction

Molecular dynamics (MD) is most useful tool for describing liquids and amorphous systems when the use of the traditional techniques is difficult [1–4]. The Newton equations of motion can be solved for a small time interval if the interaction potential and the position of  $N$  particles are given for the last points of time. Repeating this procedure the motion of the particles can be followed. There are different algorithms in the use of MD. Applying Nosé–Hoover thermostat (NH) [5,6], the temperature of the equilibrium system can be controlled. Furthermore, non-equilibrium systems can be simulated as well. In our calculations, MD simulation was performed with the tight-binding Hamiltonian of Xu et al. [7] for carbon systems. All the parameters and functions of this method were fitted to the results of local density functional calculations for graphite, diamond and linear chains. To integrate the MD equations of motion usually the Verlet algorithm [8] was used

with a time step equal to  $7.0 \times 10^{-16}$  s. Additionally, periodic and semi-periodic boundary conditions were adopted to avoid surface effects. This paper contains two main parts of our work. In the first case, we simulated the growing procedure of the amorphous carbon structure on diamond (111) surface, while in the second part, the formations of amorphous, graphite and diamond structures were studied in the bulk region.

## 2. Method

First, the formation of amorphous carbon structures was simulated on diamond-like substrate similarly to atom-by-atom deposition. In our computer experiment, there were three different sets of carbon atoms. The first one was the atomic current of initially 100 carbon atoms targeted on a (111) diamond surface. The second set was itself the substrate. It contained 54 atoms at the temperature of 0 K, where 36 out of them were in  $x$ – $y$  two planar structures, while 18 were connected to this plane from below according to  $sp^3$  geometrical layout to

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mimic the bulk. The bonded carbons with amorphous structure belong to the third set.

(a) During the procedure, a carbon atom started to move forward to the target surface. Its initial  $x$ ,  $y$  coordinates in the current were randomly defined. As the cut off distance of our tight-binding potential was 0.26 nm, to speed up the simulation, the initial  $z$  coordinates in the current were placed 0.36 nm over the target. The initial velocities of the atoms in the current were randomly determined by a temperature of 2000 K but their  $z$  component was multiplied by the factor 10 in order to produce a  $z$  directional current.

(b) If the particle arrived into a critical distance from the substrate, which was a little bit greater than the bond distance, procedure (a) started again. In the meantime, the previous particle became a member of the bonded carbons, though it kept moving. To simulate inelastic collision with the target surface, the velocity of the current atom was decreased in each MD step by a given factor.

In the second part of our work, the formation of different carbon structures in the bulk was studied. Initially, we randomly put 60 carbon atoms in a cube with a side of 12 Å with periodic boundary condition. Using the control temperature of 3500 K in a Nosé–Hoover thermostat we compressed the cube sides to 0.8424 nm, 0.800 nm and 0.64 nm. In this way, we obtained the macroscopic densities of  $\rho = 2.0 \text{ g/cm}^3$ ,  $2.335 \text{ g/cm}^3$  and  $4.56 \text{ g/cm}^3$  for the amorphous, graphite and diamond structures. In order to speed up the process of structure formation, the diamond density was higher than  $3.52 \text{ g/cm}^3$  (normal conditions). During the compression, the speed of diminishing the side was  $0.001143 \text{ nm/fs}$ . In the following 5.6 ps, the densities and the temperature were kept constant in a Nosé–Hoover thermostat.

### 3. Results

The total time of the simulation of the atom-by-atom deposition was 10 ps. In this case, the time step was  $10^{-15} \text{ s}$ . During this time 73 atoms out of 100 carbon atoms reached the region of (111) diamond surface. We used periodic boundary conditions in the  $x$  and  $y$  directions with unit vectors of  $\mathbf{a}_x = 1.28976$

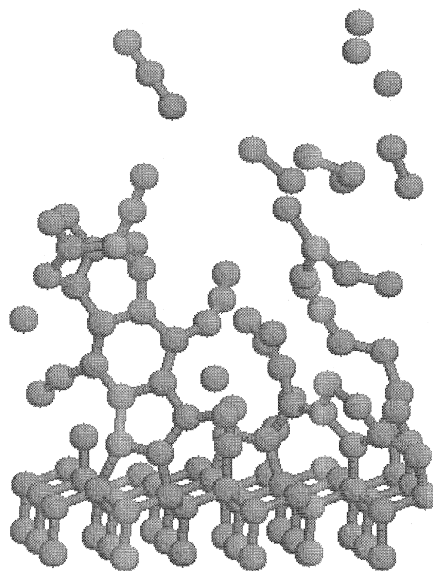


Fig. 1. The final structure in the unit cell of the atom-by-atom deposition. The 0 K target atoms are at the bottom.

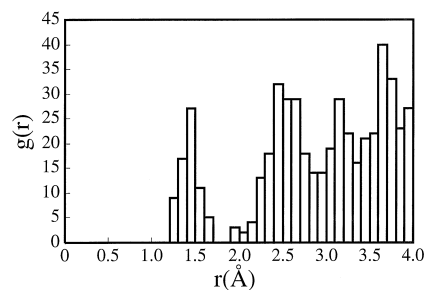


Fig. 2. The radial distribution function  $g(r)$  for the structure of the atom-by-atom deposition.

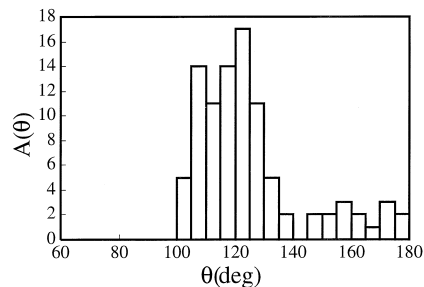


Fig. 3. The angular distribution function  $A(\theta)$  for the structure of the atom-by-atom deposition.

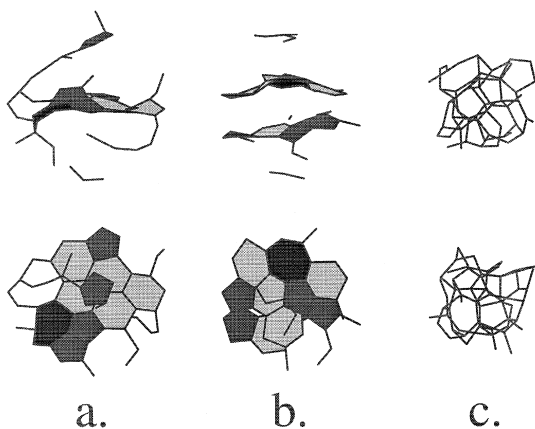


Fig. 4. The final atomic arrangement in the unit cell of the bulk structure simulation; (a) amorphous, (b) graphite and (c) diamond materials in side view (top picture) and in top view (bottom picture).

nm and  $a_y = 0.74464$  nm. The current came from the  $z$  direction. Fig. 1 shows the final structure in the unit cell and displays a chain-like amorphous structure in initial state, which contains fivefold, sixfold and sevenfold rings as well. The number of onefold, twofold, threefold and fourfold coordinated sites are 24.6%, 38.3%, 27.3% and 1.3%, respectively. In Fig. 2, we present the calculated radial distribution function  $g(r)$  in the range of 0–0.4 nm, which is close to our experimental result measured by neutron diffraction [9]. Fig. 3 shows the angular distribution function  $A(\theta)$ .

The final structures of the bulk simulation for the amorphous, graphite and diamond materials can be seen in Fig. 4. At  $\rho = 2.0$  g/cm<sup>3</sup>, an amorphous structure has been obtained with fivefold, sixfold and sevenfold rings where the atoms are arranged in distorted planes. In that case, the number of onefold, twofold, threefold and fourfold coordinated sites are 0.0%, 10.0%, 86.7% and 3.3%, respectively. In the case of graphite density  $\rho = 2.335$  g/cm<sup>3</sup>, the number of onefold, twofold, threefold and fourfold coordinated sites are 3.3%, 10.0%, 86.7% and 0.0%. Although we increased the density we did not find fourfold coordinated atoms. In Fig. 4, the distorted plane structure of graphite can be seen in initial state, which contains fivefold, sixfold and sevenfold rings. As the cut off distance of our tight-binding potential

is 0.26 nm it is a surprising fact that we have obtained a plane-like structure. When the density was increased to  $\rho = 4.56$  g/cm<sup>3</sup> the plane structure of the graphite disappeared and the tetragonal-like structure of the diamond with the (111)-like planes and the bonds that are perpendicular to these planes emerged. Now the number of onefold, twofold, threefold and fourfold coordinated sites are 0.0%, 0.0%, 10.0% and 90.0%.

#### 4. Discussions

We have presented the formation of different carbon structures under various simulation conditions. In the case of atom-by-atom deposition on diamond substrate, the final structure was a chain-like amorphous structure with fivefold, sixfold and sevenfold membered rings, while at bulk structure simulation amorphous, graphite- and diamond-like structures were found in initial states. The only difference among the three calculations is the macroscopic density which is controlled by the size of the cubic unit cell.

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