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Dynamic Properties of Disordered Phases of Carbon

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The hybrid method based on *ab initio* and empirical-potential molecular-dynamics simulations is applied to model systems for nanostructured graphite with four adsorbed hydrogen atoms to investigate the dynamic properties of the hydrogen atoms. The effects of the crystallization on the bonding states of hydrogen atoms are clarified.

Key words : carbon, dynamic properties, density-functional theory, environment-dependent potential, hybrid approach

1. INTRODUCTION

Recently much attention has been focused on the ability of the hydrogen storage of carbon-related materials with nanometer-scale, such as carbon nanotubes [1] and graphite nanofibers [2]. It is reported recently that there exists a hydrogen storage capacity of 7.4 wt.% ($CH_{0.95}$) for nanostructured graphite prepared by mechanical milling for 80 hours under a hydrogen atmosphere [3]. To clarify the microscopic mechanism of the hydrogen adsorption in nanostructured graphite theoretically, we have to treat the bonding between the hydrogen atoms and the carbon atoms in the graphite quantum mechanically and also employ a large system to take into account the 'nanostructured' graphite. For these purposes, we employ the hybrid *ab initio*/empirical-potential molecular-dynamics(MD) simulations proposed by Ogata *et al.* [4, 5], in which the system is divided into a cluster region and an environmental region. The former region is embedded in the environmental region, and the cluster atoms are treated by the density-functional theory(DFT), while atoms in the environmental region are described by the empirical interatomic potential.

In this paper, we consider the model system of the nanostructured graphite consists of five graphite layers and four hydrogen atoms which bonded to the edge sites of the central graphite layer. We apply the hybrid *ab initio*/empirical-potential MD method to this system and investigate the effects of crystallization on the bonding properties of hydrogen atoms. It is suggested from the experiments that the dissociation of hydrogen atoms occurs with the crystallization of the nanostructured graphite.

2. METHOD OF CALCULATION

In our hybrid *ab initio*/empirical-potential method [4, 5], the system (referred to as S in the following) is divided into a cluster region (referred to as C), where chemical reactions assumed to occur, and an environmental region as is shown in figure 1. Atoms in the total system are classified into three types; (i) atoms forming cluster treated quantum mechanically; (ii) atoms in the environmental region described by an empirical interaction potential; and (iii) termination atoms which terminate the cluster atoms. The potential energy of the total system is defined as follows,

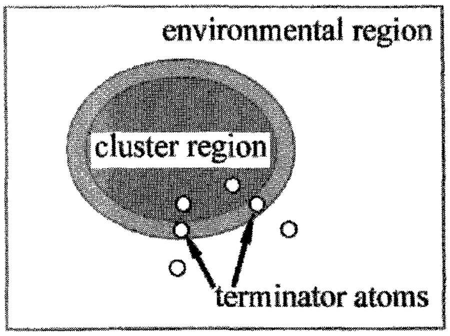

Fig. 1: The schematic picture of hybrid *ab initio*/empirical-potential method. The dark grey and white region show the cluster and the environmental region, respectively. The spheres in the light grey region represent the terminator atoms.

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

where $\boldsymbol{r}_i$ is the coordinates of the ith atom, E_{DFT} is the potential energy obtained by the DFT calculation and E_{MD} is the potential energy calculated using empirical potential. The potential energy of cluster atoms needs to be calculated by both DFT and empirical-potential calculations. The termination atoms are introduced to terminate the dangling bond of the cluster and their coordinates are given as a function of atomic coordinates in both the cluster and the environmental region.

Figure 2 shows the flowchart of the hybrid *ab initio*/empirical-potential MD simulation. The forces acting on the atoms in the cluster region are calculated by both DFT and the empirical potential, while that in the whole system are calculated by the empirical potential only.

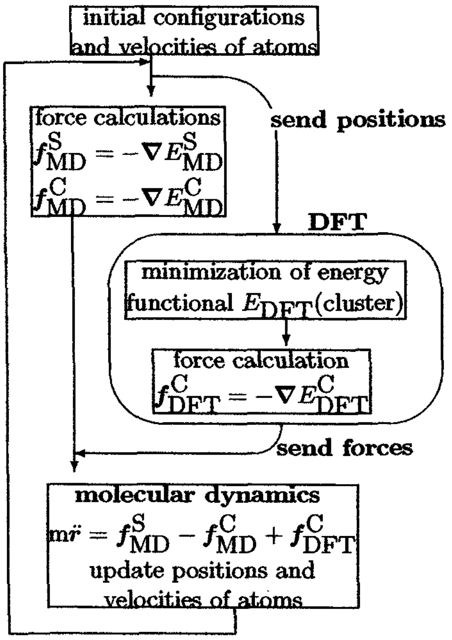

Fig. 2: The flowchart of the hybrid *ab initio*/empirical-potential method. Symbols S and C denote the system and the cluster, respectively.

In the DFT calculations, the generalized gradient approximation [6] is used for the exchange-correlation energy. The electronic wave functions and the charge density are expanded in plane waves with cutoff energies 20 and 180 ry., respectively. The energy functional is minimized using an iterative scheme based on the preconditioned conjugate-gradient method [7, 8]. The ultrasoft pseudopotential is used for interaction between valence electrons and ions[9]. The Poisson equation is solved with the real-space multigrid method [10] to obtain the Hartree potential, and the local pseudopotential is also calculated in the real space so as to avoid the interaction between the periodic replicas.

In the empirical-potential calculation, we use environment-dependent interaction potential(EDIP) proposed by Marks [11]. EDIP is represented as a sum of the pair potential and the three-body potential, and both of them 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 coordination number. Previously, we have applied the EDIP to the liquid and the amorphous carbon. Figure 3 shows the structure factors $S(k)$ obtained by our empirical-potential(EDIP) and *ab initio* MD simulations for them. The results obtained by the EDIP MD simulation agree well with the results obtained by the *ab initio* MD simulation. We have investigated the dynamic properties of the liquid and the amorphous carbon, and proved that the EDIP is able to reproduce the dynamic structures of them [12] as well as the static structures [11]. These results suggest a very good transferability of the EDIP.

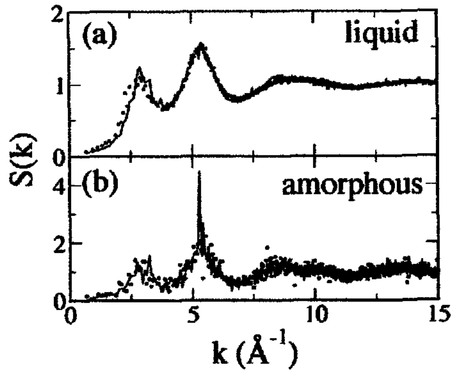

Fig. 3: The structure factors $S(k)$ in (a) liquid and (b) amorphous carbon. The circles and the lines show the results obtained by the *ab initio* and EDIP MD simulations, respectively.

We have also checked the validity of the hybrid *ab initio*/empirical-potential MD method using EDIP by applying the hybrid method to the graphite sheet(graphen) for investigating the dynamic properties such as the heat transfer [12].

3. MODELS OF NANOSTRUCTURED GRAPHITE

Figure 4 shows the model to which we apply the hybrid method. The model consists of five graphite layers and the central layer is divided into two graphite sheets. Four hydrogen atoms are bonded at the armchair edges of the left graphite sheet in central region. The system contains 1568 carbon atoms and four hydrogen atoms. The hydrogen atoms and the surrounding 32 carbon atoms are considered as the cluster region and are treated by DFT.

First, the distance between left and right graphite sheet is about 5 Å and there is no interaction between the hydrogen atoms and the right-hand carbon atoms. We carry out the hybrid MD simulation for this system (referred to as model I). Next, the right-hand sheet is shifted to left artificially to mimic the crystallization, so that the distance between two graphite sheets become about 1.5 Å, which is referred to as model II. We carry out the MD simulations again. The time step of our MD simulations is 0.97 fs and the simulation is carried out about 4.5 ps for both models. The temperature of the system is 1000K.

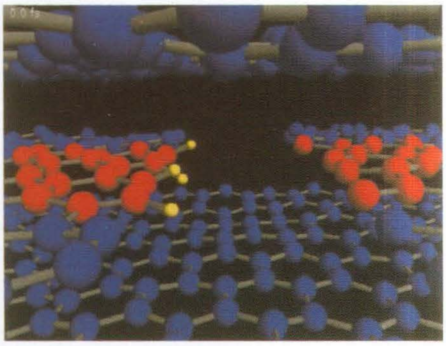

Fig. 4: The atomic configuration obtained by the MD simulation for model I. The blue and red atoms are carbon atoms calculated using the EDIP and the DFT, respectively. The yellow atoms are hydrogen atoms.

4. RESULTS AND DISCUSSION

The hybrid MD simulation is carried out for the model II. After 0.4 ps, the crystallization occurs and the hydrogen atoms are pushed by both sides of graphite sheets and move out of the sheet. Figure 5 shows the snapshot of atomic configurations obtained by the MD simulation. Three hydrogen atoms are seen above the graphite sheet and one hydrogen atom is hided below the sheet.

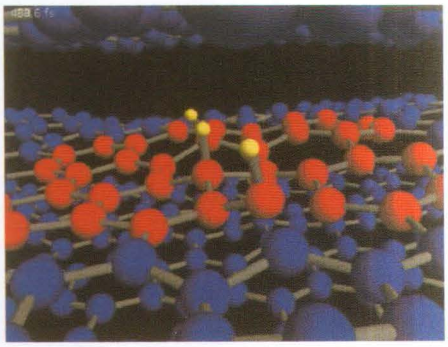

Fig. 5: The atomic configuration obtained by the MD simulation of model II.

To investigate the effects of crystallization on the dynamical properties of adsorbed hydrogen atoms, we calculate the Fourier transform of velocity autocorrelation functions(VAF) of hydrogen atoms, which is shown in Figure 6. The peaks around 3000 cm^{-1} and 1000 cm^{-1} correspond to the C-H bond stretching mode and the wagging motion of hydrogen atoms, respectively. It is seen that the frequency of the stretching mode shifts to lower frequency due to the crystallization. Though the frequency of the wagging motion remains almost same, the relative strength of the stretching and wagging motion changes due to the crystallization.

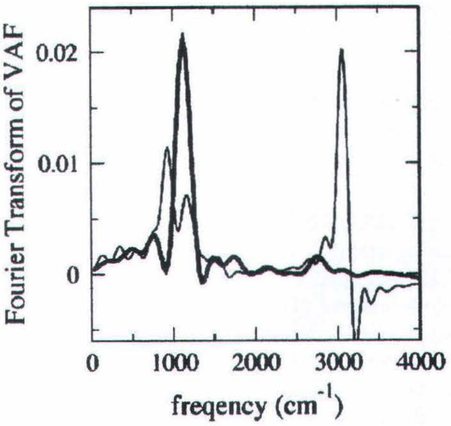

Fig. 6: The Fourier transform of the velocity autocorrelation functions of hydrogen. The thin line and the thick line show the results obtained by the MD simulations for the model I and the model II, respectively.

In Table 4. we show the bond length, the frequencies of C-H stretching mode and the bond angles related to the adsorbed hydrogen atoms before (model I) and after (model II) the crystallization. As is shown in Table 4., after the crystallization, the C-H bond length becomes longer and the frequency of C-H stretching mode becomes lower, which suggest that the bonds between the hydrogen and carbon atoms become weaker. The local structure around the carbon atoms, which are connecting with hydrogen atoms, also change due to the crystallization. After the crystallization, the C-C bond length between the carbon atom which is bonding with the hydrogen atom and the neighboring carbon atom becomes longer and the bond angle changes from about 120° (three-fold coordinates) to the smaller angle (four-fold coordinates). Note that the C-C bond length of model II is very close to that of the diamond, 1.54 Å.

5. SUMMARY

We have applied the hybrid MD simulation to the model system for the nanostructured graphite with four adsorbed hydrogen atoms to investigate the effects of the crystallization on the bonding states of hydrogen atoms. We have shown that the C-H bonds become weaker due to the crystallization in

Table I: The bond length, the frequencies of C-H stretching mode and the bond angles around the carbon atoms which is bonding the hydrogen atoms.

	model I	model II
bond length (Å)		
C-H	1.11	1.13
C-C	1.41	1.55
frequency ($\times 10^3$ cm^{-1})		
C-H	3.05	2.76
bond angle (°)		
H-C-C	119.6	101.1
C-C-C	119.5	116.0

the sense that the C-H bonds become longer and the frequency of C-H stretching mode becomes lower after the crystallization.

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