

Molecular Dynamics Simulation of the Incident Angle Dependence of Reactions between Graphene and Hydrogen Atom

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(Received 9 December 2009 / Accepted 9 March 2010)

The incident angle dependence of reactions between graphene and hydrogen atoms is obtained qualitatively by a classical molecular dynamics simulation under the *NVE* condition, in which the number of particles (N), volume (V), and total energy (E) are conserved, with a modified Brenner's reactive empirical bond-order potential. The chemical reactions depend on two parameters, the polar angle θ and azimuthal angle ϕ of the incident hydrogen. The simulation results showed that the reaction rates depend strongly on polar angle θ . The reflection rate increase with increasing θ , and the adsorption rate also depends on θ . The θ dependence is the result of the three-dimensional structure of a small potential barrier covering adsorption sites. The penetration rate also depends on ϕ for large θ .

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Keywords: incident angle dependence, molecular dynamics simulation, graphene, hydrogen, carbon, plasma wall interaction, Brenner potential, sputtering, divertor plate

DOI: 10.1585/pfr.5.S2076

1. Introduction

Carbon fiber composites (CFCs) are regarded as a candidate for the material used in divertor plates for nuclear fusion reactors, which are bombarded with hydrogen plasma. The hydrogen plasma erodes the divertor plate, yielding H_2 and other hydrocarbon molecules such as CH_x and C_2H_x , which are undesirable impurities in plasma confinement experiments. To understand the mechanism of chemical and physical interactions between hydrogen plasma and the divertor plate, the elementary processes of the reactions must be clarified. A molecular dynamics (MD) simulation, in which the equation of motion of the atoms is solved numerically, is a powerful tool for researching these processes. In previous research, we showed that the reactions depend strongly on the incident energy of the hydrogen atoms. We also clarified the physical mechanism for perpendicular injection against a graphene sheet by MD simulation [1].

The surfaces of divertor plates are no longer flat at nanoscale level. For example, CFC has a structure in which several thousand carbon fibers are twisted. The fibers have a polycrystalline structure with clusters measuring approximately 1 nm to 1 μ m, and the crystal axes of the clusters are not aligned. Moreover, single-crystalline graphite consists of multiple layers of graphene sheets. In this case, oblique incidence as well as vertical incidence should be taken into account when studying reactions with the divertor plate. In this present paper, we investigate the incident angle dependence of reactions between a hydrogen atom

and a graphene sheet by MD simulation.

The simulation method is described in section 2, and the energy dependence of the reaction rates for vertical and oblique incidences is shown in section 3. A summary is provided in section 4.

2. Simulation Method

2.1 Simulation algorithm

In this study, we used a classical MD simulation under the *NVE* condition with a modified Brenner's reactive empirical bond-order (REBO) potential [2,3]. The REBO potential is popular potential for the use in MD simulation of carbon systems. A carbon atom has four or fewer covalent bonds derived from its four valence electrons. The type of bonding depends strongly on the bonding state of the carbon atom. The REBO potential provides sufficient information on the behavior of atoms by

$$U \equiv \sum_{i,j>i} |V_{[ij]}^R(r_{ij}) - \bar{b}_{ij}(\{r\}, \{\theta^B\}, \{\theta^{DH}\})V_{[ij]}^A(r_{ij})|. \quad (1)$$

where r_{ij} is the distance between the i -th and j -th atoms. The functions $V_{[ij]}^R$ and $V_{[ij]}^A$ represent repulsion and attraction, respectively, and \bar{b}_{ij} generates a many-body force. Second order symplectic integration is used to solve the time evolution of the equation of motion [4] with a time step of 5×10^{-18} s.

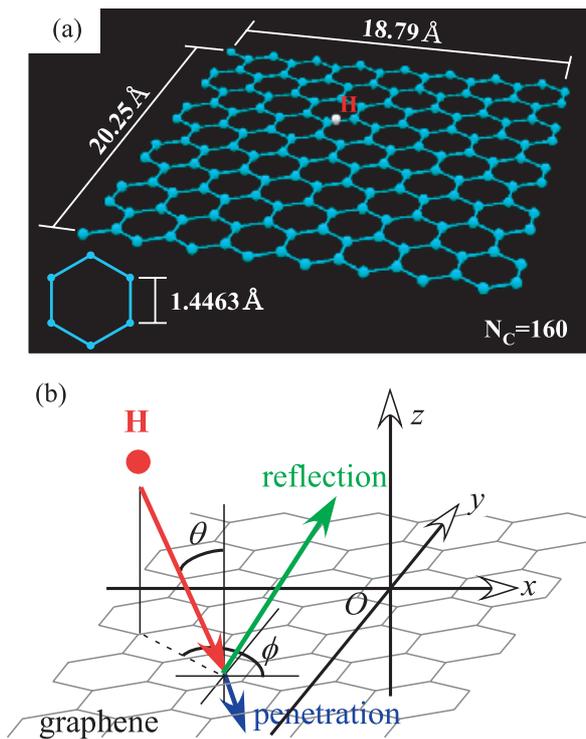


Fig. 1 (a) Simulation model and (b) the O - xyz coordinates of our simulations with polar angle θ and azimuthal angle ϕ . Origin of coordinates is set to the center of mass of the graphene.

2.2 Simulation model

As shown in Fig. 1 (a), one hydrogen atom is injected to a graphene sheet consisting of 160 carbon atoms with a periodic boundary condition in the x and y directions. The initial temperature of the carbons is set to zero Kelvin.

Figure 1 (b) shows the O - xyz coordinates of our simulations with polar angle θ and azimuthal angle ϕ . The hydrogen atoms are injected into the graphene from $z = 3 \text{ \AA}$. The x and y coordinates of the injection position of the hydrogen are set randomly. An incident angle of (θ, ϕ) is chosen. In the second simulation, we used the same simulation model except that we changed the x and y coordinates of the injection point at random before the simulation. We change the x and y coordinates of injection point randomly and start the second simulation. We repeated the above simulation 2500 times for each (θ, ϕ) individually. We observed three types of reactions; reflection, adsorption, and penetration.

3. Simulation Results

3.1 Energy dependence of reaction rate with vertical incidence

In this section, the energy dependence for vertical injection of hydrogen will be shown to compare it with the dependence for oblique injection. Figure 2 shows the incident energy dependence of the adsorption, reflection, and penetration rates for $\theta = 0^\circ$. Different interactions domi-

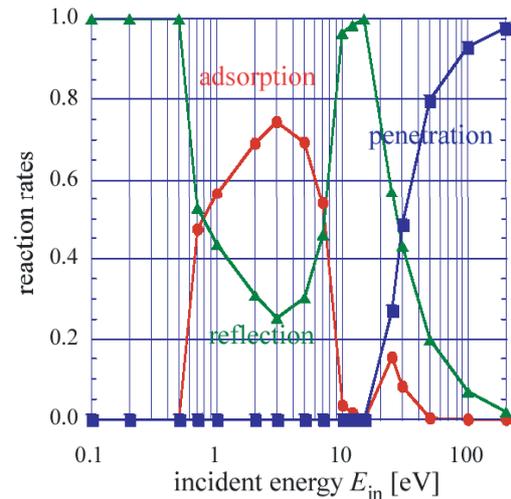


Fig. 2 Incident energy dependence of the adsorption, reflection, and penetration rates for vertical incidence.

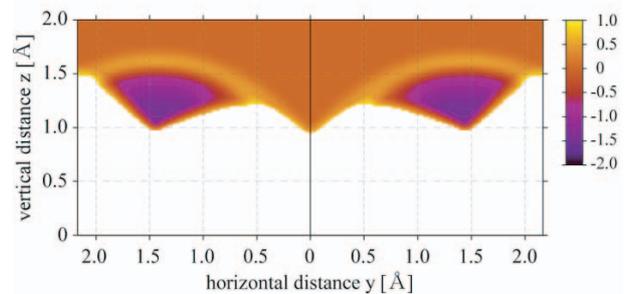


Fig. 3 Potential energy contour plot in the y - z plane that includes two adjoined carbon atoms in the graphene.

nate different incident energies E_{in} .

At low incident energy, i.e., $E_{in} < 0.5 \text{ eV}$, almost all injected atoms are reflected. To understand the physical mechanism, we drew a potential energy contour plot on a graphene sheet in the y - z plane that includes two adjoined carbon atoms (Fig. 3). The two carbon atoms are located at $(y, z) = (1.4463 \text{ \AA}, 0 \text{ \AA})$ and $(-1.4463 \text{ \AA}, 0 \text{ \AA})$. An adsorption site exists 1.1 \AA above each carbon. We found a dome-shaped, small potential barrier of about 0.5 eV , in front of the adsorption sites. Adsorbed hydrogen atoms must have a component of kinetic energy perpendicular to the tangential plane of the dome-shaped barrier, which is larger than the barrier. The three-dimensional structure of this barrier also affects the adsorption after oblique injection. We will discuss this point in detail in section 3.2. For $0.5 \text{ eV} < E_{in} < 7 \text{ eV}$, adsorption becomes dominant, but reflection becomes dominant again for $7 \text{ eV} < E_{in} < 30 \text{ eV}$. To be adsorbed at the adsorption site, hydrogen must have not only enough kinetic energy to pass the small potential barrier, but also the ability to lose its kinetic energy so that it may fall into the adsorption site by giving its kinetic energy to the surrounding carbons. Hydrogen atoms injected

directly onto carbon atoms do not have enough reaction time to lose their kinetic energy and become trapped. Increasing the incident energy shortens the reaction time, and more incident hydrogen atoms are reflected.

Penetration is the dominant process at $E_{in} > 30$ eV. At $E_{in} = 25$ eV, a second peak in adsorption is observed. This peak is caused by the back-side adsorption. In penetrating the graphene sheet, the injected hydrogen atoms lose approximately 25 eV of their kinetic energy so that they can be adsorbed on the back side of the graphene sheet.

3.2 θ dependence with oblique injection

Figure 4 shows the incident energy dependence of reaction rates on the angle θ for $\phi = 0^\circ$. The reflection rate increases with increasing θ [Fig. 4 (a)]. The rising point of the penetration rate shifts to the high-energy side with increasing θ [Fig. 4 (b1)]. This shift occurs because the vertical component of the incident energy decreases with $\cos^2\theta$. As shown in Fig. 4 (b2), the penetration rates are described as a function of $E_{in} \cos^2\theta$. In contrast, the adsorption rate cannot be written as a function of $E_{in} \cos^2\theta$ [Fig. 4 (c)]. The difference between penetration and adsorption rates differ because the latter depends on the three-dimensional structure of the potential surface on the graphene sheet. Thus the adsorption rate has a more complicated θ dependence than the penetration rate.

Figure 5 shows reaction maps for $E_{in} = 0.5$ eV, $\phi = 0^\circ$. Red dots indicate that the hydrogen atom is adsorbed. Green and blue dots denote reflection and penetration, respectively, in Figs. 5 and 7 (b). In Fig. 5, we plot “impact points” without interactions between carbon and hydrogen, which are defined by

$$\begin{pmatrix} x^i \\ y^i \\ z^i \end{pmatrix} = \begin{pmatrix} x_0^i \\ y_0^i \\ z_0 \end{pmatrix} - \frac{z_0}{v_{0z}^i} \begin{pmatrix} v_{0x}^i \\ v_{0y}^i \\ v_{0z}^i \end{pmatrix}, \quad (2)$$

where (x_0^i, y_0^i, z_0) is the initial location and $(v_{0x}^i, v_{0y}^i, v_{0z}^i)$ is the initial velocity of the i -th injected hydrogen atom. Moreover, z_0 is equal to 3 \AA for all the injections. As shown in Fig. 5, some injected hydrogen atoms are adsorbed for $E_{in} = 0.5$ eV and $\theta = 20^\circ$, although all the injections are reflected for vertical incidence. The reason is that the potential barriers around $y = \pm 0.8 \text{ \AA}$ in Fig. 3 have a minimum value of 0.45 eV. The phenomenon indicates that vertical injections to the tangential plane of the barrier are necessary to penetrate the barrier in addition to injections onto the minimum point of the barrier. At an incident energy $E_{in} = 5$ eV, the adsorption rate for $\theta = 80^\circ$ is much lower than at low θ case even though the incident energy is 10 times higher than the barrier. The small potential barrier has a dominant role at high incident energy when the polar angle θ is large.

3.3 Oblique injection - ϕ dependence

Figure 6 shows the θ dependence of reaction rates for $E_{in} = 5$ eV with several azimuthal angles ϕ . This figure

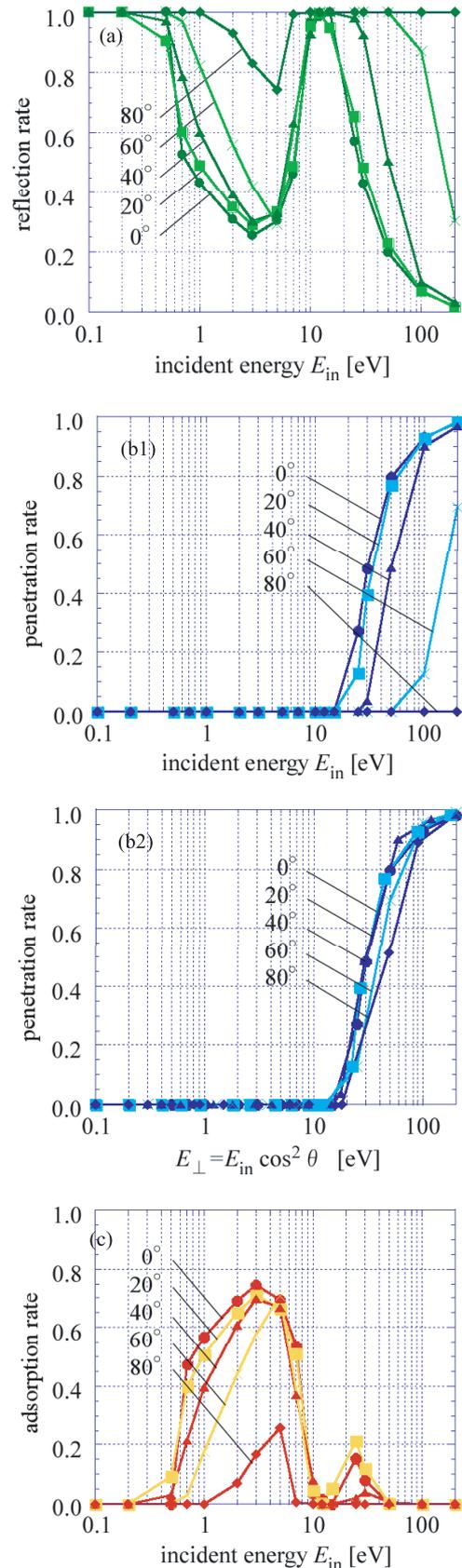
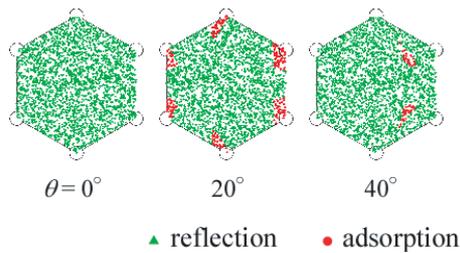
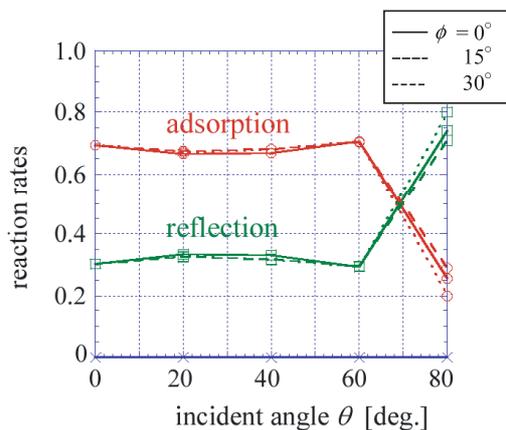
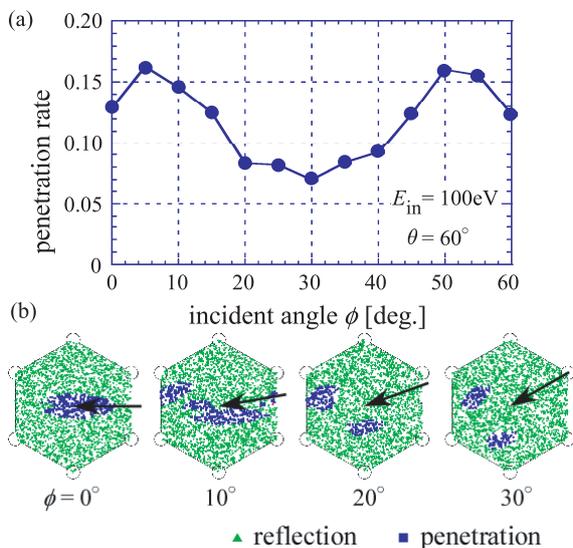


Fig. 4 Incident energy dependence of reflection (a), penetration (b1), and adsorption rates (c) with different θ for oblique incidence. (b2) Penetration rate against the vertical component of incident energy $E_{in} \cos^2 \theta$.


 Fig. 5 Reaction maps for $E_{in} = 0.5 \text{ eV}$, $\phi = 0^\circ$.

 Fig. 6 θ dependence of reaction rates for $E_{in} = 5 \text{ eV}$ with different ϕ .

 Fig. 7 (a) ϕ dependence of penetration rate and (b) the reaction maps for $E_{in} = 100 \text{ eV}$, $\theta = 60^\circ$.

shows that the reaction rates, in particular the adsorption rate, do not change by ϕ . This is because the adsorption reaction depends on the structure of the small potential barrier mentioned above, and the barrier has ϕ symmetry; that is, the graphene sheet has 6-fold rotational symmetry.

We found a ϕ dependence of the penetration rate for $E_{in} = 100 \text{ eV}$ and $\theta = 60^\circ$, as shown in Fig. 7 (a). At such high incident energy, penetration is the dominant process and the small potential barrier is regarded as negligible. Thus, the penetration process is considered to have a simple mechanism. At high energy, only the strong repulsive force near the carbon atoms contributes to bending the trajectory of the injected hydrogen. Therefore the hydrogen injected near carbon atoms is reflected, and other injected hydrogen atoms penetrate through the graphene sheet. The penetration rate decreases with increasing θ because the shadow area, which is defined as the area where the injected hydrogen encounters carbon atom increases with increasing θ . For $\phi = 30^\circ$, the shadow reaches the next carbon atom, and all injected atoms that are connected diagonally to two carbon atoms are reflected for $\theta = 60^\circ$, as shown in Fig. 7 (b). This overlapping condition of the shadow would be different for a different value of ϕ , so the penetration rate depends on ϕ when θ is large.

4. Summary

We calculated the incident angle dependence of the adsorption, reflection, and penetration rates of hydrogen atoms injected onto a graphene sheet by MD simulation. As hydrogen atoms are injected along the horizontal direction, reflection increases. The penetration rate is considered a function of the vertical component of the incident energy $E_{in} \cos^2 \theta$. The adsorption rate has a more complicated θ dependence than the penetration rate. This complexity arises from the three-dimensional structure of a dome-shaped small potential barrier about 0.5 eV high. We also found that the adsorption rate does not depend on ϕ . The penetration rate for $\theta \geq 60$ depend on ϕ .

Acknowledgment

Numerical simulations were performed using the plasma simulator at the National Institute for Fusion Science. The work was supported by the National Institutes of Natural Sciences undertaking, Forming Bases for Interdisciplinary and International Research through Cooperation Across Fields of Study and Collaborative Research Program (No. NIFS09KEIN0091) and a Grant-in-Aid for Scientific Research (No. 19055005) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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