Molecular Dynamics Study on Behavior of Hydrocarbon Molecules in Hydrogen Atom Gas

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Carbon chains are produced from a graphite (0 0 0 1) surface due to hydrogen atom sputtering. The carbon chains do chemical reaction with hydrogen ion in edge plasma. In this paper, the chemical reaction of the carbon chains in the hydrogen atom gas, which substitutes for hydrogen plasma, was investigated by the use of molecular dynamics simulation with modified Brenner reactive empirical bond order potential. In the case at temperature 10^5 K, all carbon chains were broken and they changed into atoms. In the case at temperature 10^4 K, the carbon chains changed into CH and C_2H_x molecules. In the case at temperature 10^3 K, the carbon chains brought about different reactions between the two sorts of temperature control methods. The carbon chains maintained their chain structures Langevin thermostat and thermal wall in the system of the Langevin thermostat, while the carbon chains changed into C_2H_x, C_3H_x and C_4H_x in the system of the thermal wall. This difference expects that chemical reaction in MD simulation strongly depends on temperature control method in general.

Keywords: Molecular dynamics, Carbon chain, Temperatre control, Carbon, Divertor.

1. Introduction

Hydrogen plasma bombardment onto divertor walls of nuclear fusion device causes the chemical erosion of surfaces. Because the divertor wall consists of graphitic carbon materials such as carbon fiber composite and polycrystalline graphite, the chemical erosion produces hydrocarbon molecules. Especially, H_2, CH_x and C_2H_x had been found by experiments. Because the hydrocarbon molecules have heavy mass and neutral charge, they disturb the plasma confinement in the nuclear fusion devices.

We have studied to clarify the mechanism of hydrocarbon creation on graphite surfaces using molecular dynamics (MD) simulation with modified Brenner Reactive Empirical Bond Order (REBO) potential [1, 2, 3] and interlayer intermolecular potential with cone cutoff functions [3].

In our previous works, the sort of produced hydrocarbon molecules depended on the sorts of the graphite surface. On a graphite (0 0 0 1) surface, graphenes were peeled off one by one and then many carbon chains were produced [3, 4]. In the other hand, C_2H_2 and H_2 were mainly produced on graphite armchair (1 1 -2 0) and zigzag (1 0 -1 0) surfaces, respectively [5]. However, there are a few report of the measure of the carbon chains from experimental researches. In the present paper, we simulate the behaviors of the carbon chains in hydrogen atom gas which substitutes for hydrogen plasma. Key point is the adsorption of hydrogen atom. If the carbon chains easily adsorb hydrogen atoms, adsorption energy brings about the destruction of the carbon chains.

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On the other hand, if the carbon chains easily reflect hydrogen atoms, the carbon chains can grow into large molecules. We consider that this difference is important to understand the transport and deposition of hydrocarbon molecules in the plasma shadowed area, for instance the tile gaps of divetor [6].

Moreover, we would like to examine the effect of difference between temperature control methods. There are the several types of the temperature control method in the technique of MD simulation. Because the MD simulation cannot achieve the time scale corresponding to the phenomena in experiments, some gap from real experiments appears, for example high density, high flux and so on. From this point, the cooling and heating by the temperature control methods are much stronger than that of real phenomenon. In this paper, the two types of temperature control methods are compared. One is Langevin thermostat and the other is thermal wall. The MD simulation shows that the carbon chains change into the different molecules between the systems of the Langevin thermostat and the thermal wall.

2. Simulation Methods

Initially, hydrogen atoms and the carbon chains whose edges are terminated by hydrogen atoms were placed in the simulation box at random. The simulation box has five carbon chains of the same length n. Here, the length of a carbon chain n is defined as the number of the carbon atoms in the carbon chain. That is, hydrogen atoms at the edge of carbon chain are not counted by the length n. Several MD simulations varying the length of carbon chains n from 4

Table 1: The hydrocarbon molecules in the system of the Langevin thermostat after 1 ns.

initial	Langevin thermostat		
	10^3 K	10^4 K	10^5 K
C_4H_2	3 C_4H_4	5 C_2H_2	20 C
	2 C_4H_3	1 C_2H_1	
		1 C_2	
		1 CH_2	
		2 CH	
		3 C	
C_6H_2	1 C_6H_7	4 C_2H_2	24 C
	3 C_6H_6	4 C_2H_1	
	1 C_6H_5	1 C_2	
		2 CH_2	
		4 CH	
		6 C	

Table 2: The hydrocarbon molecules in the system of the thermal wall after 1 ns.

initial	Thermal wall		
	10^3 K	10^4 K	10^5 K
C_4H_2	2 C_4H_7	4 C_2H_2	20 C
	2 C_4H_6	1 C_2H	
	1 C_2H_6	1 C_2	
	1 C_2H_2	4 C	
C_6H_2	1 C_6H_{10}	6 C_2H_2	24 C
	1 C_6H_9	1 C_2H	
	1 C_4H_6	2 C_2	
	7 C_2H_2	5 CH	
		7 C	

to 10 were performed. The positions and directions of carbon chains were set at random under uniform distribution function where the distances between the centers of carbon chains were certainly grater than $\sqrt{5} + 1.2n$ not to combine initially. At the same time, the positions of hydrogen atoms were also set at random under uniform distribution function where the distance between atoms were grater than $\sqrt{5}$. The number of hydrogen atoms was $20n$ corresponding to four times the number of carbon atoms. The simulation box is a cube whose sides are $(25n)^{1/3}$ nm. The density of atoms was kept 1.0×10^{21} atom/cm^3 in the all MD simulations. The initial momentum of hydrogen atoms obeys the Maxwell-Boltzmann distribution at the temperature T, which varies every simulation case, while the initial momentum of carbon atoms obeys the Maxwell-Boltzmann distribution at 2000 K in the all simulation cases. Temperature measured by this MD simulation is defined as $2K/3k_bN$ where K is the total kinetic energy and N is the total number of atoms, which is $25n$. The temperature of atoms was maintained at 10^3, 10^4 or 10^5 K during a simulation by the Langevin thermostat or thermal wall. This simulation was finished when the simulation time reached 1 ns.

The following approach was employed in the MD simulation. The interaction among atoms was represented by the modified Brenner REBO potential [1, 2, 3]. The modification from the original Brenner model improves the numerical accuracy on the difference calculus. In this potential model, the atoms interact only when the distance between them is lass than 2 Å. The equations of motion were solved by the symplectic integration method. The time step was 5×10^{-18} s. The temperature of atoms was controlled at T by the Langevin thermostat with simulation box satisfying the periodic boundary conditions

or the thermal wall with simulation box satisfying the non-periodic boundary conditions [7]. The random numbers were generated by SIMD-oriented Fast Mersenne Twister [8].

3. Result

The MD simulations under the following conditions revealed the temperature dependence of the chemical reaction of the carbon chains in the hydrogen atom gas. The preset temperature varied 10^3 to 10^5 K. Table 1 and 2 shows the hydrocarbon molecules in the systems of the thermal wall and the Langevin thermostat when the elapsed was 1 ns. At 10^5 K, all particle were broken into atoms. At 10^4 K, all carbon chains were broken into C_2H_x and CH. At 10^3 K, the difference between the temperature control methods occurs. The carbon chains were broken into C_2H_x and C_4H_x in the system of the thermal wall, while the carbon chains were kept their chain structure in the system of the Langevin thermostat where the number of the adsorbed hydrogen atoms increases from initial carbon chains.

To discuss the difference between the Langevin thermostat and the thermal wall, the cases of long carbon chains, C_7H_2, C_8H_2 and $C_{10}H_2$, were simulated at 10^3 K (Table 3). From this result, the long carbon chains were also kept their chain structures in the system of the Langvin thermostat. On the other hand, all of the long carbon chains were broken into the small hydrocarbon molecules such as C_2H_x, C_3H_x and C_4H_x in the system of the thermal wall.

4. Discussion

First, we discuss the temperature dependence of the chemical reaction of the carbon chains in the hydrogen atom gas. At the temperature T, the kinetic energy par one degree of freedom is evaluated by $k_bT/2$ where k_b is the Boltzmann constant. The temperature of 10^5 K corresponds to 5 eV par one degree of freedom. Since the binding energies of C-C,

Table 3 The hydrocarbon molecules after 1 ns.

chain	Langevin thermostat 10^3 K	Thermal wall 10^3 K
C_7H_2	2 C_7H_8	5 C_3H_5
	1 C_7H_7	1 C_2H_6
	1 C_7H_6	9 C_2H_2
	1 C_7H_5	
C_8H_2	1 C_8H_8	3 C_4H_7
	1 C_8H_7	1 C_2H_6
	2 C_8H_5	13 C_2H_2
	1 C_6H_3	
	1 C_2H_2	
$C_{10}H_2$	1 $C_{10}H_{10}$	5 C_3H_5
	2 $C_{10}H_9$	16 C_2H_2
	2 $C_{10}H_5$	3 CH_4

C-H and H-H bonds are smaller than 5 eV, the atoms cannot be bound by covalent bonds in the case at 10^5 K. In the cases at 10^4 K, the kinetic energy par one degree of freedom is 0.5 eV. The smallest binding energy in the covalent bonds of the carbon chain C4H2 is 2.24 eV, which is calculated by the modified Brenner REBO potential. Therefore, the kinetic energy is not enough to break the carbon chains. From the visualization of time development in the MD simulation, we found that the carbon chains were broken soon after the adsorption of the hydrogen atom. The adsorption of hydrogen atom on the carbon chain is exothermic reaction. Therefore, the adsorption energy changes into the kinetic energy of atoms to break the covalent bond. The carbon chains were split into the hydrocarbon molecules having the even number of carbon atoms such as C_2H_2 or C_4H_x according to the effect of conjugation in the carbon chains.

In the cases at 10^3 K also, the broking mechanism of the carbon chains is similar to the case at 10^4 K. Namely, the adsorption energy of the hydrogen atom is used to cut covalent bonds. However, because the kinetic energy par one degree of freedom is 0.05 eV, the ratio of the breaking is smaller than that at 10^4 K.

We here discuss the different reaction between the systems of the Langevin thermostat and the thermal wall. The carbon chains were broken in the system of the Thermal Wall, while they were kept in the system of the Langevin thermostat. This difference is caused by the difference of ways to control the temperature between the Langevin thermostat and the thermal wall. Let us begin our discussion by comparing the systems of the thermal wall and the Langevin thermostat.

In the system of the thermal wall, the atoms move as follows. When the atom bound back from the boundary of the simulation box, the kinetic energy of the atom is dumped and its velocity is sampled from the probability density of velocity as a function of preset temperature once more. That is to say, the total energy is not decreased before the atom reaches the boundary of the simulation box. The kinetic energy of the atom is, instead, controlled surely by one bounce independently of the deference of measured temperature T from the preset temperature.

On the other hand, the Langevin thermostat always works onto all atoms. Therefore, the suppression of the kinetic energy starts as soon as the chemical reaction increases the kinetic energy of atoms. The speed of suppression in the Langevin thermostat can be regulated by the register coefficient as a simulation parameter. However, if we take the fact that the kinetic energy is not suppressed at the inner space of the system of the thermal wall, the Langevin thermostat brings quickly cooling and heating. Especially, when the kinetic energy of atoms increases due to the chemical exothermic reaction, the Langevin thermostat aggressively cools the temperature of atoms.

On this consideration, we understand the difference between the temperature control methods as follows. The kinetic energy of the carbon chains was surely increased by the adsorption of hydrogen atoms. In the system of the thermal wall, the carbon chain could not dump its kinetic energy until the carbon chain reaches the boundary of the simulation box. Thereby, the carbon chain keeps high kinetic energy due to the hydrogen adsorption and then it is easily broken. In the system of the Langevin thermostat, the kinetic energy of the carbon chain was always controlled. Therefore, the carbon chain is suppressed enough to keep its chain structure before it reaches the boundary.

Let's discuss which models represent natural phenomenon well. Natural process to release the kinetic energy increased by chemical exothermic reaction are the following processes: one is the processes that the kinetic energy is diffused by the interaction between particles, the other is the process that the kinetic energy transfers into large buffer materials such as surfaces, and the last one is the process that the kinetic energy is dissipated by the frequent interaction with the background particles and field, which includes here radiation. In the system of the thermal wall, the inner space brings about the diffusion by the interaction between particles only. On the other hand, the Langevin thermostat represents the interaction with background particles and field by use of resistance and random forces, which corresponds to diffusion equation in macroscopic scale.

Because the present target is in plasma, there are many electrons as a background small particles and the electromagnetic field as a background field. This sounds as if the Langevin thermostat is suitable. How-

ever, it makes no sense at all that the electrons collides plenty during the short time of chemical reaction. The system of the Langevin thermostat corresponds to the phenomenon under the strong effect from the background particles and fields, while the system of the thermal wall corresponds to the phenomenon in a vacuum. We consider that because natural environment locates between these systems, the MD simulation controlled at preset temperature should be tried under both methods controlling temperature.

5. Conclusion

So far we have outlined the ways to control temperature using the thermal wall and the Langevin thermostat. Returning now to the chemical reaction of carbon chains in the hydrogen atom gas, we conclude as follows. Because the simulation results at 10^4 K and 10^5 K agree in hydrocarbon structures ns between the thermal wall and the Langevin thermostat, it is expected that the breaking of carbon chains into CH and C_2H_x at 10^4 K and into atoms fully at 10^5 K represents realistic reactions. For the case at 10^3 K, it is not enough to determine whether the carbon chains keep its chain structure. Rather than determining it, however, the fact that the chemical reaction is difference between the Langevin thermostat and the thermal wall is important message for whole MD simulation in chemical reaction system using the temperature control methods.

Anyway, from the present MD simulation, there is a possibility that the carbon chains produced by the chemical erosion on graphite (0 0 0 1) surfaces can changes into CH_x and C_2H_x, which are observed by the experiments on the divertor physics. This result is namely that the hydrocarbon molecule created by chemical sputtering on the graphite surface does not need to be directly desorbed from surface as CH4 and C2H6.

Finally, this comparison between the thermal wall and the Langevin thermostat implies that the different between temperature control methods causes the difference of chemical reaction in the MD simulation. This point is effective in the MD simulation of chemical erosion because the hydrogen atom bombardment is high flux and then the temperature control method must be strongly cooling.

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