EVENT-DRIVEN SIMULATION OF HYDROGEN ADSORPTION BY CARBON NANOTUBES ARRAYS WITH DIFFERENT STRUCTURES

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Hydrogen is the most energy-intensive energy source; the product of its combustion is water. One of the main obstacles to widespread use of hydrogen in the energy sector is the lack of effective methods of storage and transportation. Hydrogen can be stored as pressurized gas, cryogenic liquid, solid fuel as chemical or physical combination with materials, such as metal hydrides, complex hydrides and carbon materials, or produced on-board the vehicle by reforming methanol [1]. Transport and storage of hydrogen in the gas or liquid state in cylinders leads to a security issue. Effective way to solve this problem is to store hydrogen in carbon nanotubes, which are chemically stable, have a large surface area, a small mass and relatively inexpensive.

The US Department of Energy (DOE) published a long-term vision for hydrogen storage applications considering economic and environmental parameters. The predicted minimum hydrogen-storage capacity should be 6.5 wt% and 65 g/L hydrogen available, at the decomposition temperature between 60 and 120 ^{0}C for commercial viability [2]. Experimental results indicate that carbonaceous porous materials made up of carbon nanotubes are able to adsorb significant amount of hydrogen. The hydrogen-storage capacity for carbon materials is reported between 0.2 and 10 wt% [3–5]. On the other hand, the hydrogen adsorption characteristics were examined by molecular simulations using the Monte Carlo (MC) [6] and Molecular Dynamics (MD) [7] methods.

However, there are still many unknown questions on the mechanism of such efficient hydrogen storage. It is still argued whether the adsorption to the interior of single–walled carbon nanotubes (SWNT) or outside is more important, and whether it is simply physical adsorption or some chemical reaction is being involved.

In this paper, the physical adsorption of hydrogen molecules to a SWNTs arrays with different structures was studied by the event–driven simulation. A special attention was paid to the intrusion of hydrogen molecules in–between the SWNTs by broadening the spacing of each SWNT. Through a separate simpler simulation, the capacity of total hydrogen storage by the SWNTs arrays with different structures was calculated.

1. Simulation method. Basic methods for modeling of atomic systems have some drawbacks. For Improving accuracy of calculations requires to reduce the time step, which leads to a significant increase in the total calculation time. Besides that, using computational schemes (Verlet, Runge–Kutta), does not ensure implementation of the basic conservation laws (energy, momentum and angular momentum) in a separate act of pair interaction. This leads to the need

for additional operations for the refinement of energy, momentum and angular momentum of the system as a whole.

The event-driven method which has been used in given paper [8] generalizes the well known model of solid spheres. Model of the molecular system is a group of model particles. Model particles motion in time is described by the system of ordinary differential equations (Newton's equations of motion). The simplest piecewise constant potential was used.

Each modeled particle is modeled as two concentric spheres. Inner spheres are entirely elastic (i.e. repulsion), externals spheres – are responsible for attraction.

The events are the collisions between of inside and outside parts of model spheres. The travels are rectilinear and uniform between events. It gives us grounds to perform the process of model particles coordinate's centres changes as sequence of events, occurring in discrete moments of time. Moments of events coming are graduated in the order of their increasing. The velocities for both model particles are calculating for the event taking place in the nearest moment after the current one in accordance with requirement of conservation for pulse, total energy and angular momentum in interpartical collision. For each particle took part in collision the moments of time of new coming events at which it could take part are calculating. The least of these moments of time is introduced in events queue.

The workspace is divided into cells. New events are added. They associated with the transition of a particle from one cell to another.

We studied physical adsorption of hydrogen molecules on carbon nanotubes. Internal degrees of freedom in hydrogen molecule and the quantum effects are neglected. There are two types of interactions in the molecular system: interaction between molecules of hydrogen and carbon atoms; interaction between hydrogen molecules.

2. Results and discussions.

2.1. Parallel nanotubes arrays. We studied the physical adsorption of hydrogen in an array fragment of 19 parallel carbon nanotubes with chirality (10, 10), length $L = 3.6$ nm, and radius $R = 0.678$ nm. As the leading option the minimum distance g between the surfaces of the tubes was considered (see Figure 1). Environment settings are as follows: $P = 5$ MPa, $T = 80$ K. It was assumed that the system is enclosed in a temperature control device in which a constant temperature is maintained by scaling the velocities of the molecules.

To pressure was kept constant, using an algorithm that is in compliance with the constancy of the total number of free molecules by the addition (or exclusion) of individual particles one by one [9]. For the purposes of implementing algorithm of pressure compensation, we classify the cells as being free and occupied cells. Our implementation uses bits in the cell bitmasks to mark a cell as being free or occupied. Occupied cells surround the free cells, and they represent cells in which particles may be inserted or deleted during events to support the number of particles in free cells constant. In free cells there are

hydrogen molecules that are not associated with the carbon atoms. All free cells represent the region of pressure compensation.

The simulation was performed until equilibrium was approached, after which from the distributions of the molecular characteristics the macroparameteres were calculated.

We consider a bundle of 19 SWNTs (600 carbon atoms each), fixed the two ends. Thus, the beam is composed of infinitely long nanotubes [10]. It was assumed that the boundary conditions are reflective (or periodic, that does not lead to changes in the results).

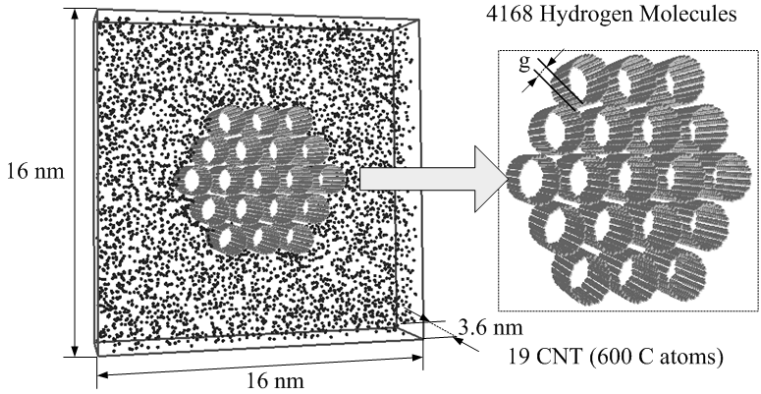

Fig.1. Geometric parameters of the array of SWNTs (g = 0.3 nm)

For a gap between the tubes of about 0.3 nm, hydrogen does not penetrate into the array and is adsorbed on its outer surface. With increase in the distance between the tubes the hydrogen penetrates into the array. When $g = 0.3$ nm the mass fraction of the adsorbed hydrogen is 1.65 wt%, when $g = 0.5$ nm – 2.37 wt%, and when $g = 0.7$ nm – 4.88 wt%.

2.2. Mutually orthogonal SWNTs. In [11] researchers have proposed a new 3D carbon nanotube matrix for storage hydrogen. They put nanotubes so they cross over each other, like the holes in a sponge. So, the tubes in this structure form the three classes, in each of which the axis of the tubes are parallel to one of the three vectors. It is suggested, that, this 3D carbon-based nanotube matrix can store and release hydrogen extremely efficiently. Hydrogen initially attaches at the points where the nanotubes touch. This doesn't occur when the nanotubes are packed in parallel with the entire edge of each tube touching others.

We consider a bundle of 19 mutually orthogonal SWNTs with chirality (10, 10) and radius $R = 0.678$ nm. As in the previous case, as the leading option we consider the minimum distance g between the surfaces of the tubes. Hydrogen molecules were initially placed at top of SWNTs as in Figure 2. It was

assumed that the boundary conditions are reflective. The calculations were performed at a temperature $T = 80$ K and a pressure $P = 5$ MPa.

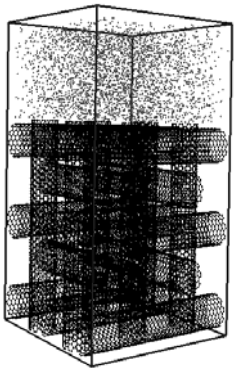

Fig.2. Initial configuration for mutually orthogonal SWNTs array ($g = 0.3$ nm)

There is no wide-open space in interior of SWNTs. Usually the both ends of as-grown SWNTs are capped with semifullerene structure. In this paper to simplify the closing free ends of SWNTs is used followed mechanism. All cells in workspace have faces that have the property of permeability or reflection. The top and side faces of the cells that cover the diametrical cross-section, which houses the final SWNT atoms are reflective in both directions. Thus, these faces make "cap", which do not allow hydrogen molecules penetrate in the SWNT.

Percentage of adsorbed hydrogen was calculated using the following formula:

$$\varepsilon = \frac{m_{finish}(H_2) - m_{start}(H_2)}{m(C)} \cdot 100\%,$$

where $m_{finish}(H_2)$ – hydrogen mass in the computational domain with SWNTs after the equilibrium, $m_{start}(H_2)$ – mass of hydrogen without the use of SWNTs under the same conditions, $m(C)$ – mass of carbon.

In the first experiment at the calculation domain measuring $8.4 \times 12.4 \times 8.4$ nm we placed an array of mutually orthogonal SWNTs with length 8.4 nm. The gap between the tubes was 0.3 nm. The upper part of the calculation domain measuring $8.4 \times 4 \times 8.4$ nm does not contain the CNT and represent the region of pressure compensation. The simulation was performed until equilibrium was approached ($t = 10000$ ps). Under these conditions the mass fraction of the adsorbed hydrogen is 9.12 wt%.

In the second experiment was studied an array of mutually orthogonal SWNTs with length 9.2 nm. Sizes of the computational domain are $9.2 \times 13.2 \times 9.2$ nm. The gap between the tubes was $g = 0.5$ nm. The simulation

time was $t = 10000$ ps. Under these conditions the mass fraction of the adsorbed hydrogen is 13.39 wt%.

In the third experiment was studied an array of mutually orthogonal SWNTs with length 13.2 nm. Sizes of the computational domain are $13.2 \times 17.2 \times 13.2$ nm. The gap between the tubes was 0.7 nm. The amount of hydrogen per unit carbon mass became about 12.56 wt%.

Figure 3 shows plots of the percentage of adsorbed hydrogen from time for various values of the gap between the tubes.

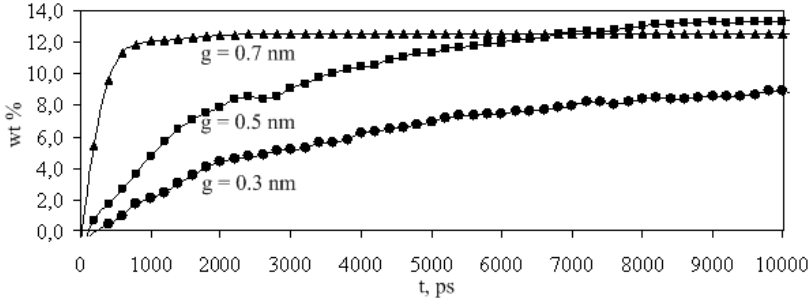

Fig.3. The percentage of adsorbed hydrogen from time for various values of the gap between the tubes

Analysis of plots at figure 3 showed that the smaller gap g, the longer the process of diffusion inside the array of SWNTs and thus time to equilibrium increases. The relative mass content of hydrogen increases with increasing gap between the SWNTs. However, for $g = 0.5$ nm maximum is observed. This fact can be explained by the formation of seals between tubes, which is absent in the case of far away tubes ($g = 0.7$ nm).

3. Conclusions. In conclusion, hydrogen fuel is clean, versatile, efficient and safe, and it will play an important role in the future world energy structure. Preliminary experimental results and some of the theoretical predictions indicate that SWNTs can be a promising candidate for hydrogen storage, which may be the solution hydrogen fuel cell-driven vehicles. Nevertheless, many efforts still have to be made to reproduce and verify the hydrogen storage capacity of carbon nanotubes both theoretically and experimentally.

In this paper we suggested the method of modeling the adsorption of molecular hydrogen in arrays of carbon nanotubes with different structures using discrete event algorithm, which reduces the computation time on a computer. Numerical calculations of the adsorption of hydrogen at a temperature $T = 80$ K and pressure 5 MPa are held. We considered an array of parallel nanotubes and mutually orthogonal nanotubes. The relative mass content of hydrogen is obtained for different distance between the tubes in the array. Array with

mutually orthogonal nanotubes can store and release hydrogen more efficiently than array with parallel SWNTs.

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