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Radius Dependence of Hydrogen Storage Inside Single Walled Carbon Nanotubes in an Array

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Abstract:
In this study, we have investigated radius dependence of hydrogen storage within armchair (n,n) single walled carbon nanotubes (SWCNT) in a square arrays. To this aim, we have employed equilibrium molecular dynamics (MD) simulation. Our simulations results reveal that radius of carbon nanotubes are an important and influent factor in hydrogen distribution inside carbon nanotubes and consequently in amount of hydrogen stored in carbon nanotube array. Moreover, our results show that the SWCNTs with radius smaller than (5, 5) SWCNTs, do not have the ability of adsorption and storage of hydrogen inside themselves.
Keywords: *Hydrogen storage, Carbon nanotube, Molecular dynamics simulation.*

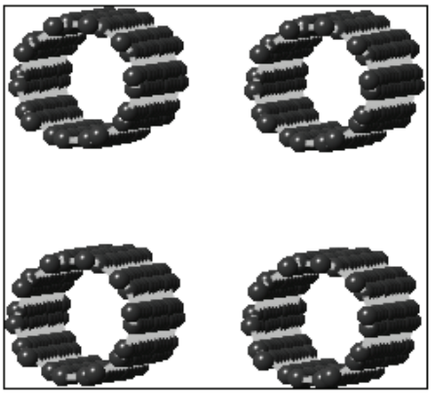
1. INTRODUCTION

Because of renewability and environmental friendly behavior, hydrogen has drawn much attention from various scientific societies as cleanest energy carrier. But there is a critical problem: low energy density. Among available technologies for hydrogen storage, it has been predicted that carbon nanotubes which were discovered by Ijima [1] in 1991, have high hydrogen adsorbents efficiency.

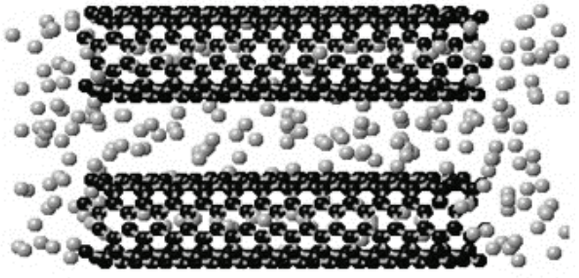
Many experimental and theoretical researchers have reported various results for hydrogen storage in carbon nanotubes [2-10]. As an example Heben and his co-workers showed that single walled carbon nanotubes (SWCNTs) can store hydrogen in the range of 5-10wt% in 133K [11] and thus can be considered as a good hydrogen adsorbent according to the US Department of Energy (DOE) standard that requires a system-weight efficiency of 6.5 wt.% [12] .

As the direct investigation of hydrogen molecular behavior in a carbon nanotube array is difficult due to the very small scale involved, numerical methods are found useful for such investigations. Furthermore, these methods can be used to clarify the best physical conditions for hydrogen storage without very expensive experimental investigations. Up to now, both Grand Canonical Monte Carlo (GCMC) [13] and Molecular Dynamics (MD) [14] simulations have been employed to investigate hydrogen molecules behavior in carbon nanotube arrays. Moreover, from Weng et al. [15] investigations, it has been cleared that storage capacity may depend on Van der Waals distance, nanotube size and arrangement of nanotubes in array. In this study, by using a different potential for H_2-H_2 interaction from that of Weng et al. [15], nanotube size effect was investigated by using of MD simulation. Our results show different behavior for Hydrogen adsorption with nanotube size that can be due to difference in interaction potential.

This paper is organized as follows. Section 2 details our simulation methodology that we use for equilibrium molecular dynamics simulation.



(a)



(b)

(c)

Figure 1: *(a) The simulation box consisting of four SWCNTs, (b) random distribution of hydrogen molecules in the box and (c) distribution of hydrogen molecules in the box after equilibration.*

In section 3, we present simulation results for the materials under investigation. Finally, section 4 provides our concluding remarks.

2. SIMULATION DETAILS

The FORTRAN code that we have used for the molecular dynamics simulation is written by our self. Figure 1 shows our simulation box which consists of four armchair (n, n) carbon nanotubes with same radiuses in a square box. In each simulation the radius of SWCNTs is different but the length of SWCNTs has a constant value of about 2.98 nm. Dimension of box is such that hydrogen molecules can enter and exit SWCNTs, freely (1.5 times SWCNT length along SWCNT axis and 6 times SWCNT radius normal to the SWCNT axis). We have used periodic boundary conditions in all three directions.

We neglected carbon atom motions in this study, because carbon atoms in SWCNT have very strong bonds and of course our simulation temperature is sufficiently low for this approximation (77K). Consequently, we need two potential functions to model H_2-H_2 and H_2-C interactions. Thus we used a Lennard-Jones potential for both of these interactions [16]:

$$U(r_{ij}) = 4\varepsilon_j \cdot \left[\left(\sigma_j / r_j \right)^{12} - \left(\sigma_j / r_j \right)^{6} \right] \qquad (1)$$

Where r_{ij} is the distance between *i* and *j* atom and σ_j and ε_{ij} are potential constants for $H_2 - H_2$ and $C - H_2$ interactions indicated in table 1.

Having the potential and forces for each atom in hand, the next step in our simulations is to integrate equations of motion for individual atoms. One of the most popular algorithms to do so, is Verlet-velocity method, which is equally accurate for nano and macroscopic systems since the particles moving out of the box with periodic boundary conditions cause no error in calculations[17]. According to this method, the positions, r, and velocities, v, of each atom are

Table 1: *Potential constants for Lenard –Jones model [16]*

Interaction/constant	σ *(Å)*	ε **(K)**
$H_2 - H_2$	2.97	33.3
$C - H_2$	3.19	30.5

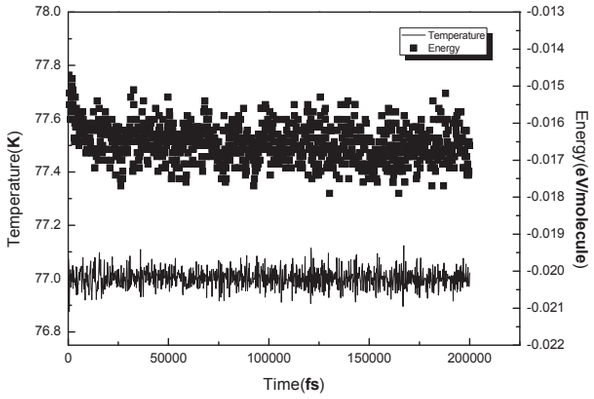


Figure 2: *The variation of total energy per molecule and instantaneous temperature of system as a function of time.*

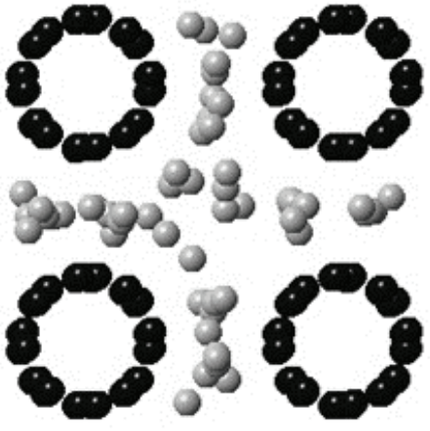


Figure 3: *The simulation box consisting of four (4, 4) SWCNTs and hydrogen molecules in the out of SWCNTs.*

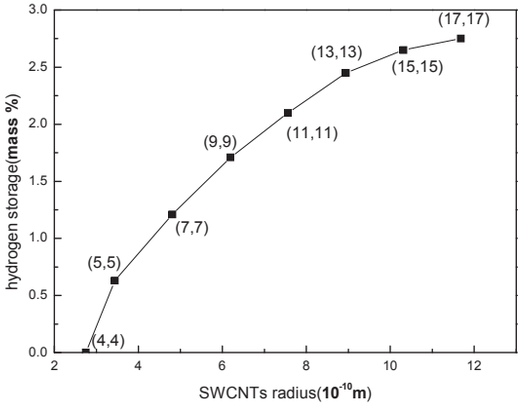


Figure 4: *Radius dependence of hydrogen storage inside SWCNTs in a square array.*

updated at each simulation time step, Δt, by:

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{(\Delta t)^2}{2} a(t)$$

$$v(t+\Delta t/2) = v(t) + \frac{\Delta t}{2} a(t) \qquad (2)$$

$$v(t+\Delta t) = v(t+\Delta t/2) + \frac{\Delta t}{2} a(t+\Delta t)$$

Where a is the acceleration of each atom.

The simulation time step Δt was set 2 *fs* to compute equations of motion and velocity scaling method to control temperature of the system. Total time of each simulation was about 200 ps. After this time, the energy profile as well as temperature (figure 2) of system fluctuates above constant values, indicating equilibration of the simulation system.

3. RESULTS

The molecular dynamics simulations were started with Hydrogen molecules located outside the nanotube close to its ends. Then, we equilibrated system during 200 *ps* and compared simulation results together. Performing similar simulation conditions for (4, 4), (5, 5), (7, 7), (9, 9), (11, 11), (13, 13), (15, 15) and (17, 17) SWCNTs revealed that SWCNTs smaller than (5, 5) SWCNT, do not have the ability of adsorption and storage of hydrogen (figure 3). Therefore, there is no justification to use these (n, n) SWCNTs for hydrogen storage.

Our observations showed that in contrast with macroscale tubes which the capacity of fluid storage (ratio of fluid mass on tube mass) is independent of their size, in this scale, hydrogen storage(ratio of hydrogen mass on SWCNT mass) is completely size dependent such that increasing SWCNTs radius leads to hydrogen storage increase inside SWCNTs and consequently in our arrays.

In figure 4, we depicted how hydrogen storage inside SWCNTs depends on radius of SWCNTs in the array. It is observed that by increasing SWCNTs radius, hydrogen storage inside SWCNTs increases. However, trend of this increase is not liner, and decreases upon radius increases. We expect this trend to be vanished after an approximate radius

reaches to macro scales. Based on our simulation results and other investigations [15] hydrogen storage between SWCNTs in an array is size independent and therefore in this paper we have just showed hydrogen storage inside the SWCNTs.

4. CONCLUSION

Molecular dynamics simulations were applied based on the Lennard-Jones potential, to investigate hydrogen storage inside single walled Carbon nanotube in a square array. Summing up the results of our MD-based simulations, we observed that the hydrogen storage within carbon nanotubes array depends on the radius of SWCNTs. Furthermore, the hydrogen storage within SWCNTs will be zero for radius smaller than (5, 5) SWCNT radius.

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