Physical adsorption between mono and diatomic gases inside of Carbon nanotube with respect to potential energy

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ABSTRACT

In this paper we have down three theoretical study by using Monte Carlo simulation and Mm+, AMBER and OPLS force field. The calculations were carried out using Hyper Chem professional, release 7.01 package of program. first we have studied the interaction of H_2 molecule and He atom with single-walled carbon nanotube at different temperature. For doing this study we placed H_2 and He in the center and outside the nanotube, permitting them to close the nearest carbon atom from nanotube. Then we plotted the potential energy versus distance of interaction, and at minimum point of energy we calculated potential energy for physical adsorption process. Second we placed tow H_2 molecules and tow He atoms at tow ends of nanotube separately, permitting them to close each other step by step then we calculated E_{kin}, E_{pot} and E_{tot} for H2---H2 and He---He interaction at different temperature. In another activity we added 2 to 100 H_2 molecules and 2 to 100 He atoms across the nanotube and after each time increased the number of H_2 and He we have estimated the potential energy, then we plotted the potential energy versus the number of H_2 molecules and He atoms so that the shape of potential curve will be determined.

Keywords: Single walled-carbon nanotube; Physical adsorption; Monte Carlo simulation; Hydrogen; Helium

INTRODUCTION

A theoretical and experimental understanding of carbon nanotubes have developed very rapidly over the last few years. The mechanical and electronic properties of carbon nanotube are interesting and give promise for useful nanotube applications in nano-engineering [1-4] and as catalyst supports [5].The unique shape of carbon nanotube useful for physical adsorption, and this paper deals with this phenomenon.

Carbon nanotubes produced by the catalytic method are believed to have close ends, composed of pentagonal and hexagonal carbon rings. The opening of the ends is achieved by cutting the tubes using an acidic and oxidizing solution with sonication [6]. studying the interaction between CNTs and mono and diatomic gases (He , H_2) could from fundamental point of view, significantly deepen our understanding on nanoscale devices physics. Single- walled carbon nanotube (SWNTs) are of interest as gas adsorbents because of their unique structural properties.

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There have been several works devoted to the investigation of the adsorption behavior of H_2 on single- walled carbon nanotube and multi – walled carbon nanotube [7-9].

In most of these researches the methods of calculations are DFT and HF. As we observe on fig. 1, the total number of carbon atoms in SWNT that we chose for study is many much, the calculations very time consuming and we need supercomputers, for resolve this problem we considered the Monte- Carlo simulation as the base of study.

The purpose of this research is studying the physical adsorption of H_2 molecule and He atom on single- walled carbon nanotube by means of Monte Carlo simulation.In this work we have modeled three different scenarios in our simulations.

In the first case, we modeled one H_2 molecule and one He atom that are located in the center and outside of the nanotube, then permitted them to close the nearest carbon atom from nanotube. In the second case we located tow H_2 molecules (or tow He atoms) at the ends of the nanotube and allowed them to close each other, then the H_2---H_2 and He---He interaction at the different temperatures were determined separately. In the third case, we entered H_2 molecules (or He atoms) to the nanotube, then the interaction energy of H_2 molecules (or He atoms) with nanotube by Monte Carlo method were determined. These calculations also were carrying out with additional 2 to 100 H_2 molecules (2 to 100 He atoms) to nanotube.
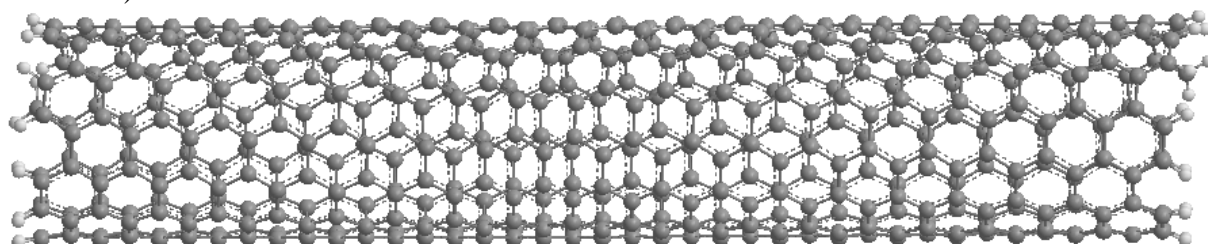
THEORETICAL BACKGROUND

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in wich a substance diffuse in to a liquid or solid to from a solution. the term sorption encompasses both process, while desorption is the reverse process.

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purifications. Similar to surface tension, adsorption is a consequence of surface energy, in a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled but atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms, that it is energically favorable for them to bond with whatever happens to be available, the exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorptions.

Physisorption: or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through van der waals (weak intermolecular) interactions, which are also responsible for the non- ideal behavior of real gases.

Fig. 1. The structure of carbon nanotube that we chose for study in this paper.

Chemisorption: is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the van der waals forces which cause physisorption.

Adsorption is usually described through isotherms, that is functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption, namely freundlich isotherm, Langmuir isotherm, etc.

Theoretical details
1) as we know, in order to carrying out any quantum mechanical calculation in Hyper Chem7.0 program package there are three steps [10]. first, prepare a molecule with an appropriate starting geometry. Second, choose a calculation method and its associated (set up menu) options. Third, choose the type of calculation (single point,geometry optimization, molecular dynamics, langevindynamics, Monte Carol and vibrational analysis) with the relevant (compute menu) options.

These geometry optimization calculations can use either molecular mechanics or quantum mechanics to further refine the molecular geometry beyond that given by the Model Builder. Hyper Chem uses the metropolis method [11], wich choose random configurations with this probability, to concentrate sampling of configurations in regions of space that make important contributions to the calculation of thermodynamic averages.

Molecular Mechanics (Monte Carlo simulation)
2) Monte Carlo is a term used in many field of science, engineering, statistics and mathematics to mean entirely different things, the one (and only) thing that all Monte Carlo methods is that they all use random numbers to help calculate something.

Monte Carlo simulation are widely used in the field of chemistry, biology, physics and engineering in order to determine the structural and thermodynamics properties of complex system at the atomic level. Thermodynamics averages of molecular properties can be determined from Monte Carlo methods, as can minimum – energy structures [12-13].

Also, it should be noted that constraining potentials (wich keep the cluster components from straying too far from a cluster's center of mass) are sometimes used[14]. At finite temperature, clusters have finite vapor pressures and particular cluster sizes are typically unst able to evaporation. Introducing a constraining potential enables one to define clusters of desired sizes.

The Monte Carlo method is one of the most broadly and commonly used numerical technique, with application in statistical physics, quantum mechanics, field theory and others [15]. Monte Carlo simulation which can generate a canonical ensemble, is applied when systems have difficult integrals to be solved and should generate some random number to generate uniform independent values statistically [16-17]. In the Monte Carlo method a metropolis algorithm is applied more than other algorithm because of its simplicity [18]. the accuracy of the algorithm is determined by random displacement in trivial displacements, all moves can be accepted, but in large cases the rate of acceptable moves is small.

In this investigation, the calculations of the interaction between mono and diatomic gases with single- walled carbon nanotube by Mm+, AMBER and OPLS force field have been performed. in this investigation Hyper Chem professional release 7.01 is used for the quantum chemical calculations, we have performed geometry

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optimization and Monte Carlo simulation by this software.

RESULT AND DISCUSSION

In the studies of H_2 on larger diameter carbon nanotube tow adsorption state were reported. One is the physisorption and the other one is a chemisorptions stat [19-21]. In the chemisorption state the H_2 molecule dissociates and adheres on two adjacent C atoms on the outer wall of tube.

Before any calculation we must answer tow questions (i) does H_2 like to be physically adsorbed on or to be chemically dissociated adsorbed on SWNTs? (ii) and if H_2 is dissociated adsorbed on tube , does it destroy the tube's structure?

In the recent years, several first principles calculations have shown that H_2 molecule is difficult to dissociate on graphen or nanotube. Arellano et al.simulated the reaction of H_2 on (5, 5) an (6, 6) tubes in details and found that the estimated energy barrier for H_2 dissociated on these tubes are greater than 2.5 ev [18-20]. Hence in this article we choose the H_2 physisorption for study. theoretical calculations of H_2 adsorption on SWCNTs have been performed using various methods.

Ab intio simulations that indicate the potential for higher uptake are subject the tight- binding or density functional approximations is not expected to be accurate for physisorption [22-23].

In this research we placed H_2 molecule (and He atom) out of and inside of the SWCNT, them we chose nearest carbon atom from the wall of nanotube and while H_2, step by step approaching to the nano tube, potential energy has been calculated. after this we have plotted potential energy as a function of distance, and at the minimum point of energy (D_{min}) physisorption has been calculated by the following relation:

$$E_{ads} = E_{SWNT-H2} - (E_{SWNT} + E_{H2})$$

Where $E_{SWNT-H2}$ is the potential energy of the optimized SWNT-H_2, E_{SWNT} is the potential energy of the optimized SWNT and E_{H2} is the potential energy of the isolated H_2 molecule.

In table 1 and 2 we show the calculated potential energy of physisorption at different temperatures when H_2 and He placed inside and outside of the nanotube.

It is found from table 1 and 2, when temperature increases the potential energy of physical adsorption process, also increase and with change in the temperature and force field the position of minimum points also changes. Like wise in this article, in addition to the physical adsorption we have studied the H_2---H_2 and He---He interaction inside of SWNT by Mm+ , AMBER and OPLS force field in different temperature (290, 294, 298, 302, 306, 310). in order to do this, first we placed tow H_2 molecules(and tow He atoms) at the tow ends of the nanotube ,second we put them closer together step by step by gauss view softwar, then we calculated kinetic energy (E_{kin}), potential energy (E_{pot}) and total energy (E_{tot}) by Monte Carlo simulation (see table.3.4,5). in (Fig. 2) E_{kin} changes calculated versus different temperature by Monte Carlo simulation and Mm+ , AMBER and OPLS force field.

As shown in (Fig. 2, 3) with increasing temperature, kinetic energy also increases, the largest amount of kinetic energy is observe at 310K and kinetic energy and potential energy for He---He interaction is greater than H_2---H_2 interaction but in calculations with Mm+ force field, potential energy and kinetic energy for H_2---H_2 interaction is greater than He---He interaction.

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Table 1. Eads (in kcal/mol) in the adsorption process of H_2 and He on external wall of nanotube calculated by Monte Carlo and Mm+, Amber and Opls force field

Temperature(K)			250	270	290	310	330	350
H_2	Mm+	$D_{min}(A°)$	5	4.5	2.5	2	3	3
		Eads	342.18	381.31	451.14	422.37	466.12	504.26
	Amber	D_{min}	4.5	3	4.5	3	3	3
		E_{ads}	349.16	381.13	488.78	431.17	455.11	476.5
	OPLS	$D_{min}(A°)$	2.5	2	4	2	5	4
		E_{ads}	357.66	378.13	400.02	428.67	474.91	482.02
He	Mm+	$D_{min}(A°)$	3.5	2.5	5	4	4.5	3
		E_{ads}	382.06	399.05	423.18	448.91	488.82	523.36
	Amber	$D_{min}(A°)$	3.5	1.5	1	1	2	3
		E_{ads}	410.46	437.47	448.8	482.22	506.21	535.82
	OPLS	$D_{min}(A°)$	3	1	2.5	3.5	3.5	3.5
		E_{ads}	365.17	411.22	437.19	466.64	487.1	537.99

Table 2. E_{ads} (in kcal/mol) in the physical adsorption process of H_2 and He on internal wall of nanotube calculated by Monte Carlo and Mm+,Amber and OPLS force field

Temperature(K)			250	270	290	310	330	350
H_2	Mm+	$D_{min}(A°)$	4.5	4	3	4.5	2	4
		Eads	357.79	371.41	393.72	434.9	472.16	489.27
	Amber	$D_{min}(A°)$	3.5	3	4.5	3	2	1.5
		E_{ads}	346.03	387.3	393.89	420.23	434.52	464.04
	OPLS	D_{min}	2.5	3.5	4	1.5	4	3
		E_{ads}	345.49	365.06	392.32	430.85	429.25	467.85
He	Mm+	$D_{min}(A°)$	1.5	2	2.5	3	2	2.5
		E_{ads}	356.81	368.88	404.01	455.4	459.29	477.74
	Amber	$D_{min}(A°)$	4.5	4	2	2	3.5	2
		E_{ads}	395.94	421.65	455.31	478.63	499.56	529.53
	OPLS	$D_{min}(A°)$	1.5	4.5	3.5	1.5	1.5	3.5
		E_{ads}	367.77	396.86	446.54	458.53	500.14	503.46

Table 3. The kinetic energy (E_{kin}), potential energy (E_{pot}) and total energy (E_{tot}) calculated for H2---H2 and He---He interaction inside of SWNT by Monte Carlo simulation and Mm+ force field in different temperature

gases	Monte Carlo/Mm+						
	Temperature(K)						
	E(kcal/mol)	290	294	298	302	306	310
H2	Ekin	466.79	473.23	479.67	486.11	492.54	498.98
	Epot	2359.77	2365.74	2381.64	2383.44	2387.64	2394.48
	Etot	2826.36	2838.98	28861.31	2869.55	2880.12	2893.47
He	Ekin	465.7	471.47	477.89	484.31	490.72	497.14
	Epot	2368.84	2372.15	2371.5	2382.3	2395.15	2388.94
	Etot	2833.9	2843.63	2849.4	2866.61	2885.87	2886.08

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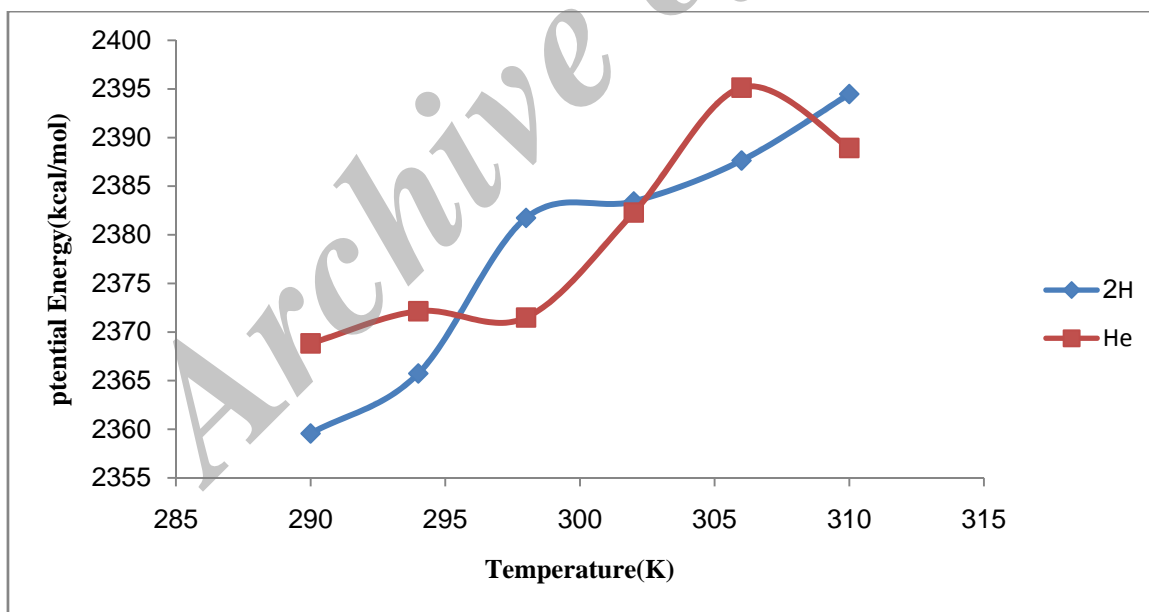
Table 4. The kinetic energy (E_{kin}), potential energy (E_{pot}) and total energy (E_{tot}) calculated for H2---H2 and He---He interaction inside of SWNT by Monte Carlo simulation and Amber force field in different temperature

gases	Monte Carlo/Amber					
	Temperature(K)					
	E(kcal/mol)	290	294	298	302	306	310
H2	Ekin	442.59	448.69	454.8	460.9	467.01	473.11
	Epot	1099.7	1104.52	1095.83	1103.08	1136.2	119.611
	Etot	1542.29	1553.21	1550.63	1563.98	1603.2	1592.72
He	Ekin	465. 06	471.47	477.89	484.31	490.72	497.14
	Epot	1144.73	1157.16	1158.57	1168.86	1162.35	1178.25
	Etot	1609.78	1628.64	1636.46	1653.17	1653.07	1675.4

Table 5. The kinetic energy (E_{kin}), potential energy (E_{pot}) and total energy (E_{tot}) calculated for H2---H2 and He---He interaction inside of SWNT by Monte Carlo simulation and opls force field in different temperature

| gases	Monte Carlo/opls					
	Temperature(K)					
	E(kcal/mol)	290	294	298	302	306	310
H2	Ekin	442.59	448.69	454.8	460.9	467.01	473.11
	Epot	1586.11	1593.24	1612.94	1608.23	1613.64	1630.39
	Etot	2028.7	2041.93	2067.74	2069.13	2080.65	2103.5
He	Ekin	465. 06	471.47	477.89	484.31	490.72	497.14
	Epot	1613.87	1616.6	1623.8	1630.54	1633.18	1624.12
	Etot	2078.93	2111.52	2101.69	2114.85	2123.9	2169.16
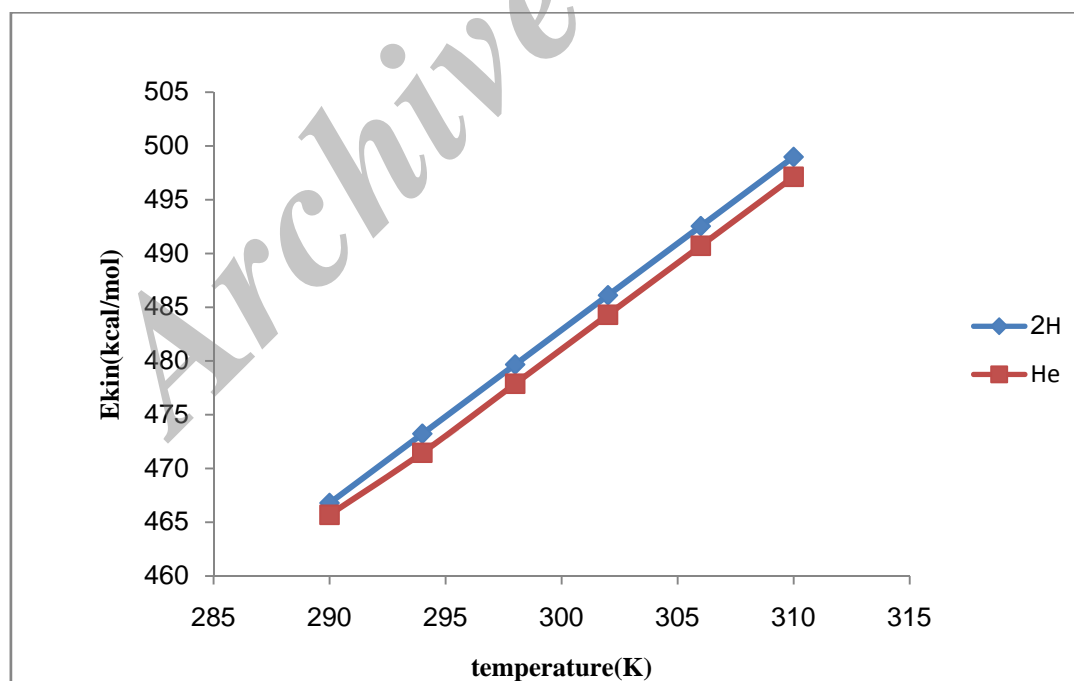
Fig. 2. *E* kin changes (kcal/mol) calculated versus temperature for H2---H2 and He---He interaction inside of SWNT by Monte Carlo simulation and Mm+ force field.
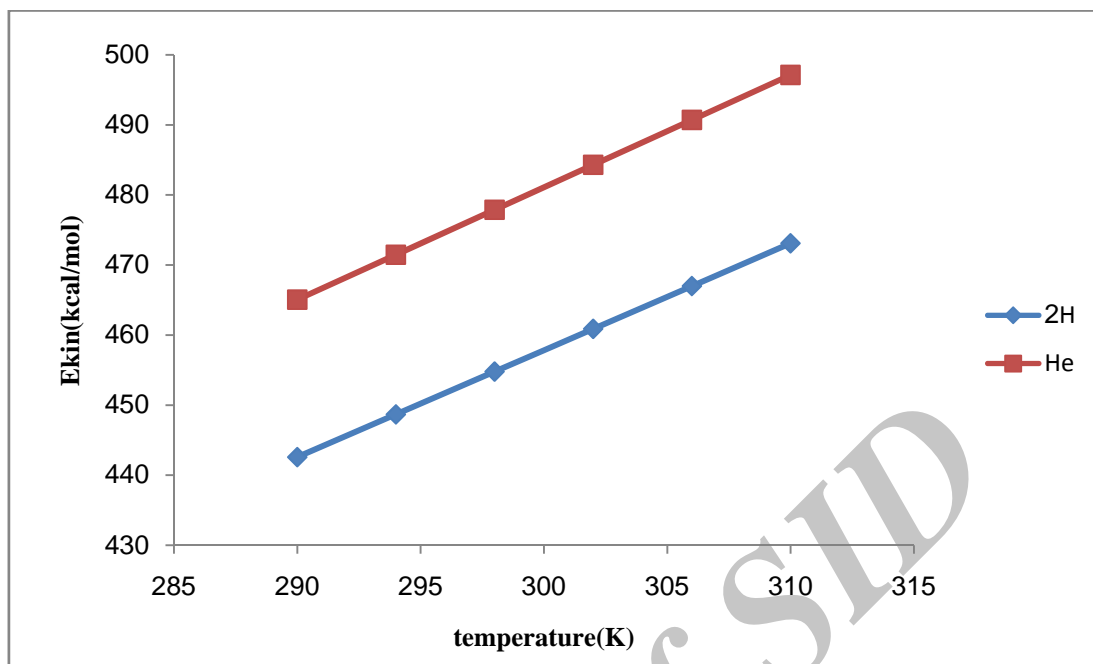
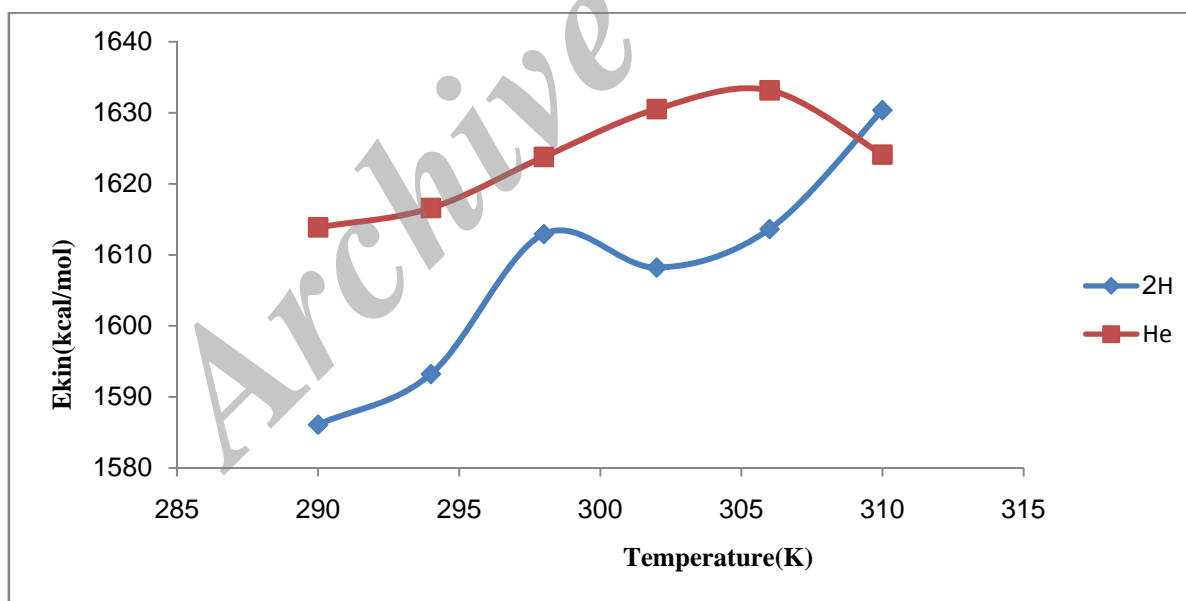**Fig. 3.** *E* kin changes (kcal/mol) calculated versus temperature for H2---H2 and He---He interaction inside of SWNT by Monte Carlo simulation with Amber and opls force field.

Fig. 4. *E* pot changes (kcal/mol) calculated versus temperature for H2---H2 and He---He interaction inside of SWNT by Monte Carlo simulation and Mm+ force field.
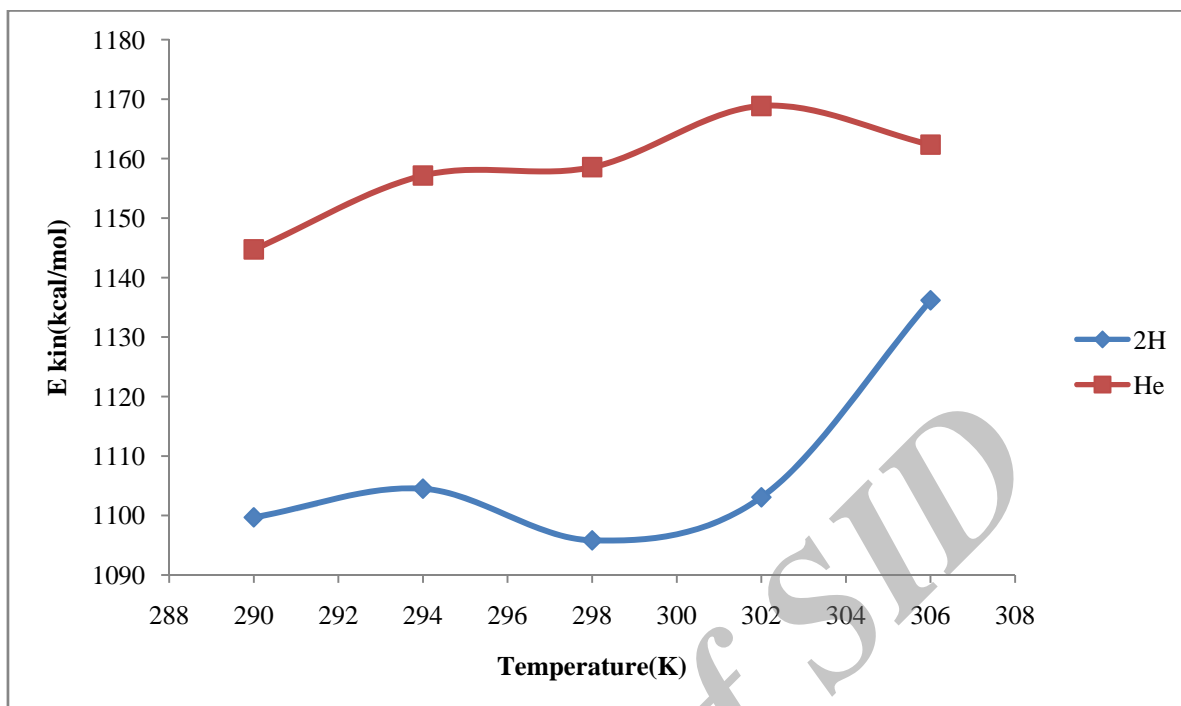
Fig. 5. *E* pot changes (kcal/mol) calculated versus temperature for H2---H2 and He---He interaction inside of SWNT by Monte Carlo simulation and Amber force field.

Fig. 6. *E* pot changes (kcal/mol) calculated versus temperature for H2---H2 and He---He interaction inside of SWNT by Monte Carlo simulation and opls force field.

In another activity, we placed from 2 up 100 H_2 molecules (2 up 100 He atoms) across the SWCNT, and after each time we incrased the H_2 and He, we have estimated the potential energy by the following relation:

$$Ep = \frac{(E_{SWCNT-nH2}) - E_{SWCNT}}{n}$$

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Where $E_{SWNT-nH2}$ is the potential energy of the single- walled nano tube with H_2 molecules or with He atoms, E_{SWCNT} is the potential energy of the optimized single-walled nanotube and n is the number of H_2 molecules or He atoms added to the nanotube. after that, we plotted the potential energy versus the number of H_2 or He, so that the kind of potential curve will be determined, (see fig. 7-10).

Paying careful attention to the diagrams reveals that changes of temperature do not cause any considerable changes in potential energy.
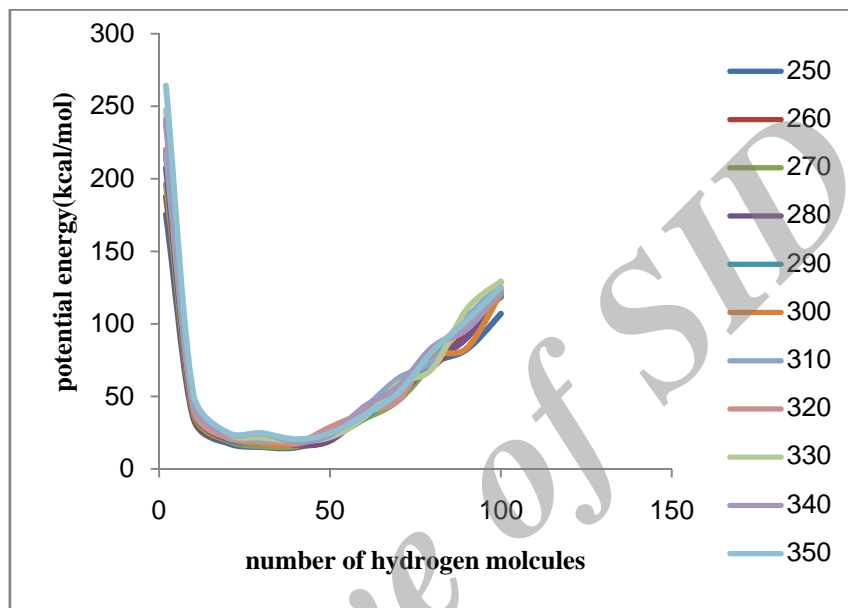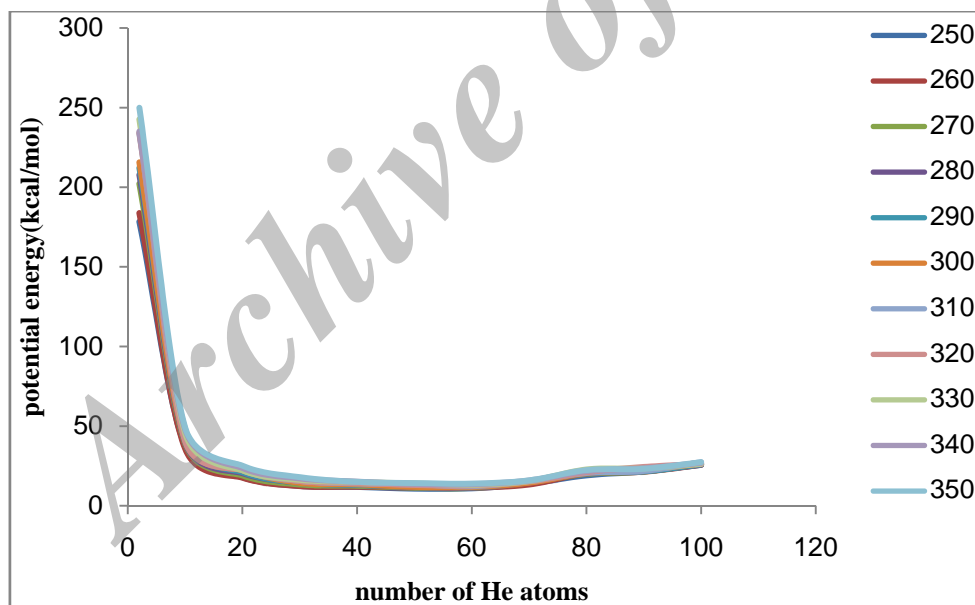

Fig. 7. potential energy curve versus number of H_2 molecules added to SWCNT by Monte Carlo simulation and Mm+ force field.
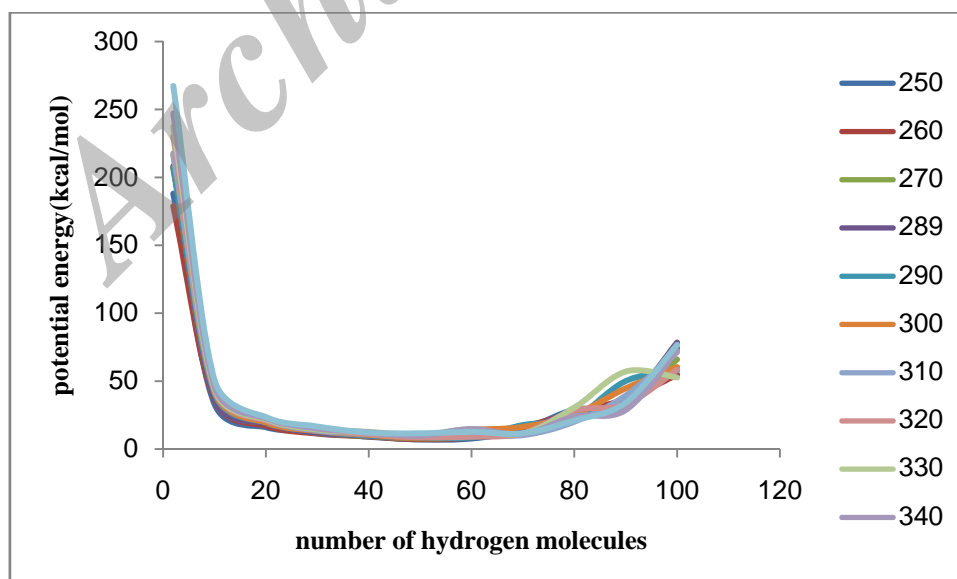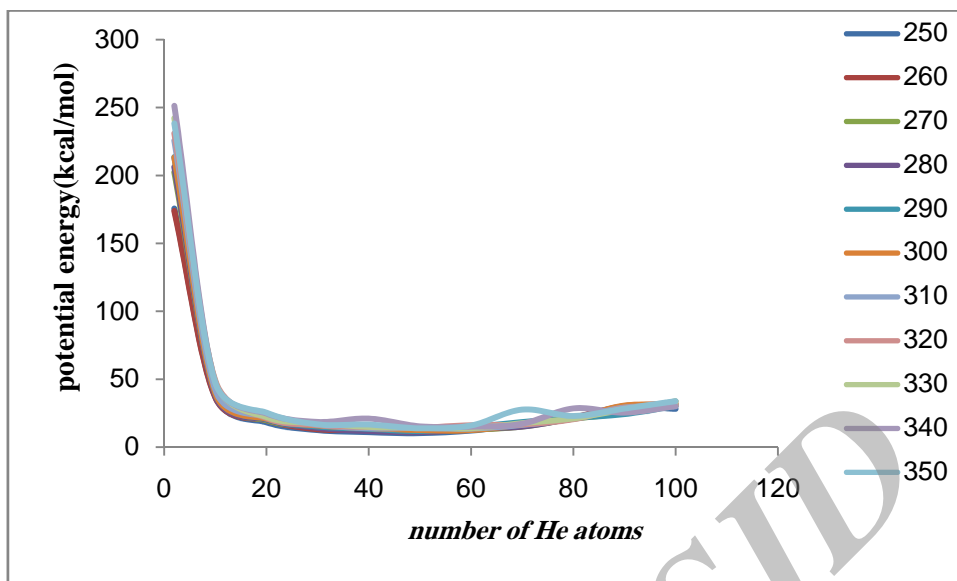

Fig. 8. potential energy curve versus number of H_2 molecules added to SWCNT by Monte Carlo simulation and Amber force field.
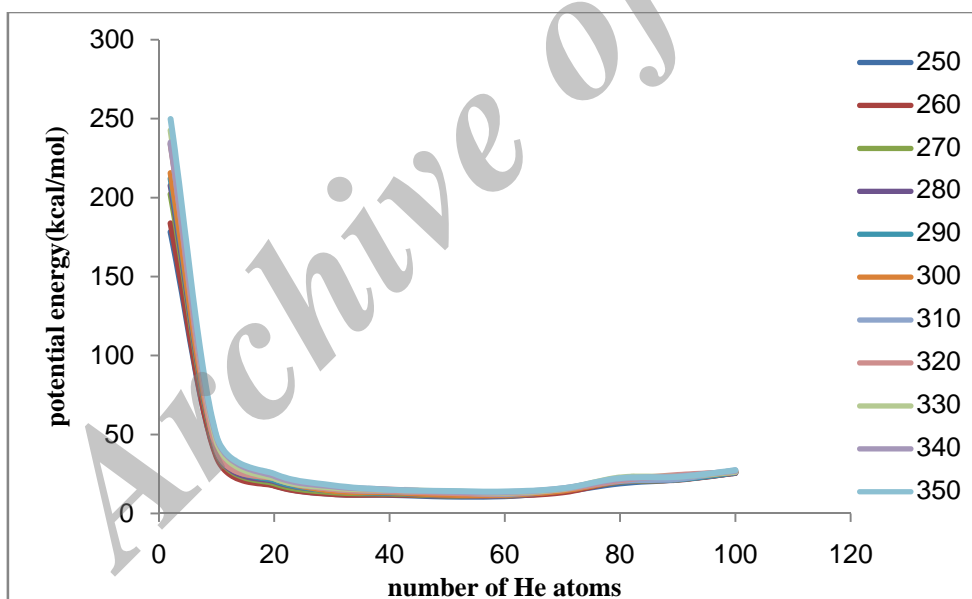
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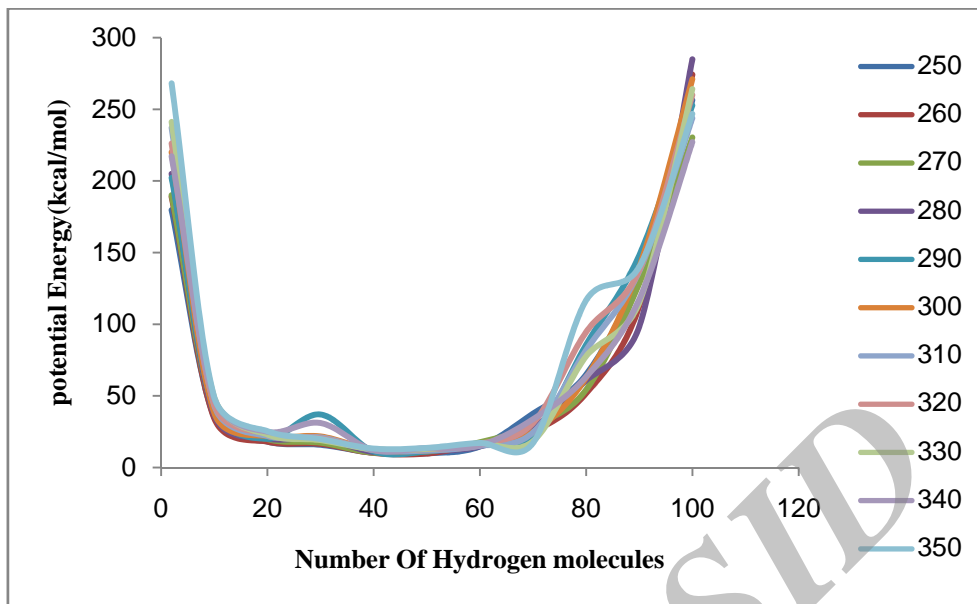
Fig. 9. Potential energy curve versus number of H_2 molecules added to SWCNT by Monte Carlo simulation and OPLS force field.

Fig. 10. Potential energy curve versus number of He added to SWCNT by Monte Carlo simulation and Mm+ force field.

Fig. 11. Potential energy curve versus number of He added to SWCNT by Monte Carlo simulation and Amber force field.

Fig. 12. Potential energy curve versus number of He added to SWCNT by Monte Carlo simulation and opls force field.

CONCLUSION

In this paper physical adsorption properties for H_2 and He on single walled carbon nanotube have been investigated using Monte Carlo simulation and different force field (AMBER, OPLS, Mm+). the calculated parameters are the potential energy of H_2 and He with inside and outside wall of single walled carbon nanotube. 1t is found that the interaction of H_2 and He with SWNT is depend to changes of temperature, but changes of force field does not cause any considerable

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change in potential energy. In addition of H_2 to SWNT the diagrams indicate that when the number of He atoms increase the interaction between tube and He atoms decreases, but in the case of H_2 the interaction energy first decreases and then increases.

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