

High Adsorptive Property of Opened Carbon Nanotubes at 77 K

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Hydrogen adsorption in porous materials is one of the methods actively being studied to store hydrogen on board vehicles driven by fuel cells. Recent experiments and numerical simulations have shown that adsorbent materials appropriate to hydrogen storage could be made up of carbon nanotubes. In this work we study the properties of such materials. By Monte Carlo simulations, we compute the hydrogen adsorption in two arrangements of opened single-walled carbon nanotubes at a temperature of 77 K and pressures up to 15 MPa. A quantitative comparison is made between simulation data and experimental results. The studied nanotube arrangements seem able to adsorb hydrogen gas in amounts required for their use in fuel cell vehicles.

1. Introduction

Among the efficient ways to store hydrogen, the formation by chemisorption of metallic hydrides is inconvenient in that gas desorption requires high temperatures, and liquefaction has the disadvantage of occurring at very low temperatures. At room temperature, gas compression is only useful for pressures above 50 MPa. Thus, hydrogen adsorption seems to be the unique possibility for storage at low and moderate pressures under 20 MPa in a wide temperature range from 77 to 300 K. The difficulty of this latter method lies in finding appropriate adsorbent materials. Although the problem of achieving optimal synthesis and purification of sizable amounts of carbon nanotubes remains unsolved,¹ experimental and theoretical works have shown that efficient adsorbent materials could be made up of carbon nanotubes. This possibility has motivated much research on the use of carbon nanotubes to store hydrogen gas for practical purposes, for instance, in fuel cell vehicles. The references^{2–6} and the present work are examples of such research.

At a room temperature of 293 K, it was demonstrated in refs 2 and 7–10 and also in refs 3 and 5 that hydrogen was efficiently adsorbed in carbon nanotube materials made up of lattices of tubes with adequate diameters. In the articles,^{3,5,11} by using grand canonical Monte Carlo (GCMC) simulations, hydrogen adsorption was computed in nanotube arrangements of parallel tubes composing a two-dimensional lattice. At moderate pressures, the amount of gas stored by adsorption in a volume filled by nanotubes was larger than that stored by gas compression in the same volume. It was maximal in a hexagonal configuration of nanotubes with diameter equal to 1.2 nm and distance from 0.7 nm. At a pressure of 10 MPa and a temperature of 293 K, volumetric density storage of 11 kg m⁻³ was obtained for tubes with diameters of 1.957 nm spaced from 0.7 nm. Comparisons between the gas adsorption rates in single-walled carbon nanotube (SWNT) lattices and stacks of graphite

basal planes separated by slits of width ~ 0.7 nm were also performed. These stacks of graphite planes, which remain theoretical and hypothetical models of porous materials, present adsorptive properties even better than those of SWNT lattices because of an easier access of gas molecules to the attractive adsorbent surfaces.

The efficiency of adsorption is frequently expressed in the gravimetric density unit kg kg⁻¹ (noted wt %), that is, in the present case, the mass of hydrogen adsorbed per mass unit of adsorbent material. This unit has been used by the Department of Energy (DOE) to define a minimal hydrogen adsorption of 6.5 wt % for a material convenient for practical applications. Recently, at a temperature of 77 K, a value of 8.25 wt % was measured for hydrogen adsorption in carbon nanotubes,⁶ higher than the minimal value defined by the DOE. The main purpose of the present work is to perform a comparison of these experimental results with GCMC simulation data, to test that these simulations are able to give an acceptable estimate of hydrogen adsorption in nanotube materials.

To accurately compute hydrogen adsorption at low temperature, it does not seem possible to neglect the quantum effects. Path-integral formalism in conjunction with the Monte Carlo method (PIMC) is an exact way to take into account these effects. Path-integral formalism for the computation of equilibrium properties of quantum systems at finite temperature is well-described in the literature, for instance, in ref 12. It has been applied in ref 13 to compute the properties of a cluster of hydrogen molecules at 6 K. From these simulations, it was demonstrated that, for temperatures above 20 K, PIMC methods are not needed to estimate quantum effects in hydrogen fluid. At these temperatures, the Feynman–Hibbs (FH) perturbative approach, which uses the expansion parameter $\hbar/(k_B T m_{H_2} \sigma_{H_2-H_2}^2)$ (m_{H_2} and $\sigma_{H_2-H_2}$ mass and size of the hydrogen molecule and k_B Boltzmann constant), seems sufficient to calculate, with reasonable uncertainty, the quantum contribution to hydrogen adsorption. At room temperature, such a computation has already been realized in ref 5 for various structures of nanotube networks by GCMC simulations; it showed that the

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TABLE 1: Hydrogen Adsorption Data at 77 K and up to 15 MPa in Carbon Nanotubes Arranged in Square and Hexagonal Lattices^a

Lattice	V^*	D	d	P	\bar{N}_{Quant}	ρ_{ads}^*	\bar{N}_{Comp}	ρ_{comp}^*	\bar{N}_{Class}
Square	3496.7	1.2	0.7	1	1031.2	0.294	90.9	0.026	1240.1
	3496.7	1.2	0.7	4	1241.6	0.355	384.6	0.110	1452.6
	3496.7	1.2	0.7	7	1302.0	0.372	692.3	0.198	1526.8
	3496.7	1.2	0.7	10	1337.0	0.386	979.1	0.280	1572.2
	3496.7	1.2	0.7	13	1369.9	0.390	1223.8	0.350	1604.9
	3496.7	1.2	0.7	15	1382.3	0.393	1353.2	0.387	1613.9
	8367.6	1.9	0.7	15	3426.6	0.409	3238.2	0.387	4037.8
	9674.6	1.9	0.9	15	4083.8	0.422	3744.1	0.387	4830.9
	11076.4	1.9	1.1	15	4566.0	0.412	4286.5	0.387	5594.1
	11911.5	2.2	0.9	15	5050.7	0.424	4609.7	0.387	6060.4
	13461.8	2.2	1.1	15	5586.7	0.415	5209.7	0.387	6797.9
	5383.6	1.2	0.7	1	1688.5	0.313	139.9	0.026	1995.6
	5383.6	1.2	0.7	4	1863.5	0.346	592.2	0.110	2181.9
	5383.6	1.2	0.7	7	1921.4	0.357	1065.9	0.198	2226.3
Hexagonal	5383.6	1.2	0.7	10	2001.4	0.372	1507.4	0.280	2327.3
	5383.6	1.2	0.7	13	2008.8	0.373	1884.2	0.350	2344.0
	5383.6	1.2	0.7	15	2033.6	0.378	2083.4	0.387	2346.0
	14895.1	1.9	0.9	15	6477.6	0.435	5764.4	0.387	
	17053.3	1.9	1.1	15	7292.0	0.427	6599.6	0.387	
	18339.0	2.2	0.9	15	7935.6	0.432	7097.2	0.387	
	20725.8	2.2	1.1	15	8801.6	0.424	8020.8	0.387	

^a V^* , the volume of the simulation cells expressed in reduced units $V^* = V/\sigma_{\text{H}_2-\text{H}_2}^3$. Tube diameters D (nm). Tube spacing d (nm). Gas pressure P in MPa. \bar{N}_{Quant} is the average number of gas molecules present in the cell containing the nanotubes taking into account quantum effects. \bar{N}_{Comp} is the average number of the gas molecules that should be present by gas compression in volume V^* of an empty simulation cell. \bar{N}_{Class} (column 10) is the average number of gas molecules adsorbed without taking account quantum corrections. Densities $\rho_{\text{ads}}^* = \bar{N}_{\text{Quant}}/V^*$ and the bulk density ρ_{comp}^* equal to $\bar{N}_{\text{Comp}}/V^*$. The numbers of carbon atoms present in simulation cells for square and hexagonal material configurations and used to estimate gravimetric densities wt % are $N_{\text{square}}(D = 1.2 \text{ nm}) = 3744$, $N_{\text{square}}(D = 1.9 \text{ nm}) = 7200$, $N_{\text{square}}(D = 2.2 \text{ nm}) = 8348$, and $N_{\text{hexagonal}}(D = 1.2 \text{ nm}) = 6642$, $N_{\text{hexagonal}}(D = 1.9 \text{ nm}) = 12800$, $N_{\text{hexagonal}}(D = 2.2 \text{ nm}) = 14848$.

quantum corrections were less than 5%. At a temperature of 77 K, where the FH expansion parameter is equal to 0.036, a rough estimate of the increase of quantum contributions on the basis of the ratio of temperatures 298 K/77 K, indicates that these contributions should be on the order of 20%.

The article is organized as follows. In section 2, we summarize our numerical simulation procedure and describe the interactions involved in the computation of hydrogen adsorption in SWNTs. In section 3, we discuss our simulation results and compare them with those recently obtained experimentally on SWNTs by Ye et al.⁶

2. Simulation Procedure

Hydrogen adsorption in SWNTs has been computed in two arrangements of opened carbon nanotubes by GCMC simulation, a Monte Carlo method well-adapted to the study of adsorption process.¹⁴ These arrangements were, respectively, a square and a hexagonal lattice of 9 and 16 parallel SWNTs disposed in a parallelepipedic simulation cell with periodic boundary conditions. Following the diameter and spacing of the tubes, the sizes of the cell sides varied between 3 and 10 nm and the number of carbon atoms present in the cell between 4000 and 15 000. The configurations of hydrogen molecules in the lattices were generated by attempting to insert, to delete, and to displace H_2 molecules in the simulation cell with an equal probability and accepting the new configurations in accordance with their GC probability weight and the Metropolis algorithm.

The Lennard-Jones (LJ) potentials were used in the simulations to describe the H_2 – H_2 and H_2 –carbon interactions. The LJ parameters of the H_2 – H_2 potential were equal to $\sigma_{\text{H}_2-\text{H}_2} = 0.2958 \text{ nm}$ and $\epsilon_{\text{H}_2-\text{H}_2} = 36.7 \text{ K}$ and those between the carbon atoms in the nanotubes and hydrogen molecules equal to $\sigma_{\text{C}-\text{H}_2} = 3.179 \text{ nm}$ and $\epsilon_{\text{C}-\text{H}_2} = 32.056 \text{ K}$. In addition to the LJ interaction between the gas molecules, the H_2 – H_2 quadrupole interaction was considered similarly to the procedure used in ref 5.

Because the quantum contributions to adsorption are a priori on the order of 15–25%, the FH effective potential,¹⁵ computed at the first order in h^2 from the LJ potentials, remains acceptable for estimating them with good precision (cf. the value of the FH expansion parameter quoted above for $T = 77 \text{ K}$). At this order in h^2 , the quantum effects are determined only from the LJ interactions, with the contribution of the quadrupole interaction being negligible.

3. Results

The simulation results in the square and hexagonal lattices of SWNTs are given in Table 1. We used opened SWNTs, which, in the two adsorbent arrangements, allowed gas adsorption both inside and outside the tubes. The nanotubes had diameters D equal to 1.2, 1.9, and 2.2 nm and were distant from each other by a spacing d equal to 0.7, 0.9, and 1.1 nm. As the gravimetric density is an important criterion for evaluating hydrogen storage efficiency, we express hydrogen adsorption ability of the SWNT lattices in gravimetric density units wt %. In Table 1, we give the computed average number of adsorbed gas molecules \bar{N}_{Quant} in the simulation cell of volume V , taking into account quantum effects, and the molecule number \bar{N}_{Comp} of a compressed gas in the same volume and in the same thermodynamic conditions. \bar{N}_{Comp} is equal to $\rho_{\text{H}_2} V$ where ρ_{H_2} is the bulk gas density at 77 K and considered pressures. From \bar{N}_{Quant} and \bar{N}_{Comp} , we estimate the ability of the SWNT lattices to increase or decrease the hydrogen amount available in V with respect to the amount present in V by gas compression. \bar{N}_{Class} , the average number of gas molecules computed without quantum corrections, differs from \bar{N}_{Quant} , as expected, by 15–20%, in agreement with the hypothesis that they could be estimated by a perturbative approach. But these effects are significant, and cannot be neglected in the estimation of the gas adsorption in the range of temperature 70–140 K.

At room temperature, where the effect of the gas-adsorbent attractive interaction is rapidly damped with the distance, the

hexagonal arrangement adsorbs hydrogen more efficiently than the square lattice, because the hexagonal lattice is more compact. Indeed, at 293 K the gas adsorption occurs within one layer near the gas-adsorbent interface, because the effect of the attractive interactions is limited to this distance range. Thus, maximum adsorption occurs at low tube diameters ($D = 1.2$ nm) and low intertube spacings ($d = 0.7$ nm). At 77 K, the effect of attractive interactions are such that two layers of adsorbed gas may occur both inside the tubes and between the nearest neighbor tubes (cf. ref 11). Thus, at 77 K, the highest adsorption rates are obtained for two-times larger tube diameters and spacings and less compact nanotube lattices than at 293 K.

For the different nanotube arrangements, the adsorption obtained at 77 K both in the square and hexagonal lattices is larger than that found at 293 K, because the low temperature reinforces the effect of gas-adsorbent attractive interactions. Hydrogen adsorption is generally more important when SWNTs are arranged in a square lattice than in the hexagonal case, because of the highest volume available for gas molecule adsorption in the square lattice (cf. the remark above). At 10 MPa and 77 K, simulations predict maximal hydrogen adsorption in SWNTs of diameter $D = 2.2$ nm and spacing $d = 1.1$ nm equal to 11.24 wt %, a value nearly twice as large as the value required by DOE and corresponding to a ratio of hydrogen atoms to carbon atoms H/C equal to ~ 2 . At this maximal adsorption, the volumetric density (mass of gas adsorbed per volume unit) reached is about 60 kg m^{-3} , a value close to that required by the DOE (62 kg m^{-3}). This adsorption rate is the highest found for carbonaceous adsorbents,^{2,6,9,11,16} with the exception of graphite nanofibers, where the noncorroborated result H/C equal to 24 has been reported in ref 17. The present amount of adsorbed hydrogen could still be slightly increased by a systematic search for the best opened SWNT arrangement, tube diameter, and intertube spacing.

Our present simulation results are in agreement with the experimental adsorption measurements in SWNTs performed at 77 K and up to 10 MPa recently published by Ye et al.⁶ In these experiments, hydrogen adsorption is equal to 8.25 wt % at 10 MPa, a value smaller than that computed by simulation (11.24 wt %). The difference between these values is attributed to the fact that, in the simulations, gas adsorption takes place outside and inside carbon nanotubes of identical diameters disposed in a perfect lattice configuration. Both simulation and experimental values of the gravimetric density are higher than the DOE target quoted above.

As shown in Table 1, when we increased the tube diameter from $D = 1.2$ to 2.2 nm and the tube spacing from $d = 0.7$ to 1.1 nm, the number of adsorbed hydrogen molecules varied because of the increase in the adsorbing surface and the volume part occupied by hydrogen at bulk density. Whereas the first change in the adsorbing surface is favorable to the increase in adsorption efficiency, the second one in the volume is unfavorable. These competitive effects are illustrated in Table 1 by computing the hydrogen densities in the simulation cell when it is filled by adsorption in the presence of the two SWNTs lattices: ρ_{ads}^* (column 7 of Table 1) and is filled by compression without adsorbent: ρ_{comp}^* (column 9 of Table 1). At low tube spacing equal to 0.7 nm, we also noticed that hydrogen adsorption could be reduced by steric effects, which precludes the localization of two layers of adsorbed H_2 molecules between nearest-neighbor carbon nanotubes.

At constant tube spacing $d = 0.7$ nm and different tube diameters $D = 1.2$ and 1.9 nm, we saw a slight improvement in gas adsorption; the density ρ_{ads}^* of adsorbed H_2 molecules

increased from 0.393 to 0.409. At constant tube diameter $D = 1.9$ nm and increasing tube spacings $d = 0.7, 0.9$, and 1.1 nm, we also obtained a similar increase of ρ_{ads}^* from 0.409 to 0.412. The densities of the adsorbed gas, expressed in reduced units of $\rho_{\text{H}_2-\text{H}_2}^3$, reached 0.386 and 0.424 at 10 and 15 MPa when the tubes were arranged in the square lattice because of the large volume available to gas molecules outside the carbon nanotubes (cf. remarks above). It is remarkable that the densities of adsorbed gas obtained at 10 and 15 MPa corresponded to those that would be obtained by gas compression at 15 and 18 MPa, leading to an increase due to the adsorption effect, in the available gas amounts by 50 and 20% at these pressures.

At room temperature (293 K) and moderate pressures (up to 12 MPa), an adsorption of 4.2 wt % has recently been obtained with purified SWNTs. This value corresponds to a physical adsorption of about 3.2 wt %⁹ since the gas chemisorption was evaluated as contributing by 21.7% to total adsorption. This experimental adsorption result 3.2 wt % can be compared with simulation data previously obtained at 293 K in ref 5 equal to 1.6 wt %. The origin of the discrepancy equal to 1.6 wt % is difficult to determine. In the experiment, gas adsorption was estimated by monitoring the decrease in the gas pressure in the cell containing the SWNTs versus time. Such a process of adsorption measurement will be valid only if the whole pressure decrease has taken place at constant temperature, a point that is not clearly stated in ref 9. If the experimental value 3.2 wt % is considered as granted, this would imply that the hydrogen-carbon potential model used in the simulation would underestimate the attractive interaction between H_2 molecules and carbon atoms in the nanotube wall. It is puzzling that this misestimate of the hydrogen-carbon interaction does not seem to exist at low temperature, because good agreement was obtained between the present simulation data and experimental results of ref 6.

4. Conclusion

At 77 K and moderate pressure, we demonstrated that SWNTs exhibit excellent properties of physical adsorption that show a value of computed gravimetric density storage equal to 11.24 wt %. The latter value leads to the conjecture that these nanoscale-dimension materials could play a determining role in the improvement of hydrogen storage by adsorption. Comparisons between our numerical simulations and recent experimental results have clearly shown the possibility of adsorbing large hydrogen amounts in SWNTs at 77 K.

Although the description of the hydrogen-carbon interaction in terms of LJ potentials should probably be improved to obtain full quantitative agreement between experimental and simulation results, our data show that the simulations are able to estimate with acceptable accuracy the adsorption properties of nanotube material at moderate pressures and in a large range of temperature (77–293 K).

We think that higher adsorption rates could still be reached by studying other nanotube geometric configurations different from those considered. Indeed, as we illustrated with several examples in this work, slight variations in the tube diameter and tube spacing can substantially increase gas adsorption. One possibility for optimizing hydrogen adsorption in tubular adsorbent is to consider materials made of multiwalled carbon nanotubes. The attractive gas-adsorbent interaction resulting from the multilayered structure of nanotube walls should increase gas adsorption near the gas-solid interface. Other possibilities such as those using doped or charged carbon nanotubes obtained by electrochemical modifications of the

carbon nanotubes should locally increase the gas-adsorbent interaction and allow higher gas adsorption.

Certainly, further investigations are needed to estimate and measure accurately the hydrogen adsorption in carbon nanotube materials. But it already seems clear that these materials should enable a very significant improvement in hydrogen storage by adsorption and could be used in clean systems supplied by fuel cells.

References and Notes

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