Monte Carlo simulations of hydrogen storage in carbon nanotubes

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Abstract
The storage capacities of porous materials made up of carbon nanotubes are estimated by Monte Carlo simulations for the specific case of hydrogen in the pressure domain from 0.1 to 20 MPa at temperatures of 293, 150 and 77 K. The use of these materials in devices for hydrogen storage is discussed on the basis of the simulation results.

1. Introduction

The study of the fluid adsorption in carbonaceous porous materials has been for many years an area of active experimental and theoretical research. This interest, motivated by the use of this process in industrial applications, has been recently reinforced by the search for ways to safely and effectively store hydrogen with a view to common use of fuel cells on board cars. To operate under conditions of speed and range similar to those of present-day cars, fuel-cell-powered vehicles must have a tank capable of containing a few kilograms of hydrogen. Most cars have tanks capable of containing ~ 0.06 m^3 of gasoline, corresponding to an available energy of $\sim 1.8 \times 10^6$ kJ. A similar amount of energy is obtained from the reaction $2H_2 + O_2 \rightarrow 2H_2O$ in a fuel cell by using ~ 15 kg of H_2.

The current technologies for hydrogen storage are: liquefaction, compressed gas, chemisorption in metal hydrides [1, 2] and physisorption in porous solids [3–5]. The density of hydrogen liquid is 71.1 kg m^{-3} at a pressure of 0.1 MPa and temperature of 20 K. This temperature rules liquefaction out for storing hydrogen for a long period. A pressure of 20 MPa and room temperature seems adequate for the storage of hydrogen since the density of hydrogen is 14.4 kg m^{-3} in this thermodynamic state. However, the weight of an empty tank made up of steel storing ~ 10.0 kg of hydrogen in these physical conditions is of the order of 500 kg. The amount of hydrogen adsorbed in the metal hydrides at room temperature and a pressure of 0.1 MPa is ~ 20–50 kg m^{-3}, but the densities of these adsorbents, 6–9 g cm^{-3}, and their costs seem too high for mobile storage of hydrogen on board vehicles; however, they are acceptable for static storage where, in particular, the weight is not a decisive constraint [2].

Physisorption seems an interesting alternative to the storage methods mentioned above. New types of activated carbons, with specific surface areas, measured by the BET procedure, as large as $\sim$3000 m^2 g^{-1} and graphite nanofibres have been synthesized and their adsorption properties have been measured [6–8]. In addition, experimental results indicate that carbonaceous porous materials made up of carbon nanotubes are able to adsorb significant amounts of hydrogen [9–16].

Since the structure of nanotube walls, which are rolled up basal planes of graphite, is known and the interaction between hydrogen molecules and carbon atoms located in nanotube walls is described by van der Waals pair interactions, a credible determination of the adsorption properties of carbon nanotube porous materials seems possible by using numerical simulations.

It is the aim of this work to present and to compare new results and previous results obtained in [11, 17–20] via numerical simulations on the adsorption properties of carbon nanotubes. The paper is organized as follows. In section 2, the models of the porous materials used in the simulations and the simulation procedures are briefly described. In section 3, the results of the simulations are given and discussed. These results allow us to reach a conclusion, presented in the final section, regarding the use of carbon nanotubes for the storage of hydrogen on board vehicles.

2. Models and simulations

The porous materials made up of carbon nanotubes are obtained by arc discharge evaporations. For the synthesized samples, transmission electronic microscopy shows that the nanotubes are aligned and packed to form ropes [21]. For a theoretical study of these materials, it seems appropriate to consider that the nanotubes are parallel and arranged in a regular array. The carbon nanotubes can be single-walled or multi-walled. In the first case, the wall of the nanotubes is made up of a basal plane of graphite rolled up into a cylinder; in the second case the wall is made up of a stack of basal planes of graphite rolled up into a cylinder. The porous materials of single-walled nanotubes with open ends seem promising adsorbents. The solid part of the materials is reduced to the adsorbing surface. Hydrogen can be adsorbed on the internal and external surfaces of the tubes. Due to the limited range of the attractive van der Waals interaction between hydrogen molecules and carbon atoms, the adsorption is not very much increased if the nanotubes are multi-walled. It is mainly determined by the attraction induced by the carbon atoms of the graphite plane constituting the external or internal surfaces of the tubes.

A simple and ideal model of nanotube materials consists of parallel single-walled nanotubes with equal diameters D on a two-dimensional triangular lattice where the minimal distance between the nanotube walls is equal to d. In the cylindrical wall obtained by rolling up a basal graphite plane, the carbon atoms form a two-dimensional hexagonal lattice where each carbon atom has three nearest neighbours at a distance $c \simeq 1.42$ Å. The diameter D of a nanotube is equal to $D = c\sqrt{3}/\sin(\pi/n)$ where n is the number of hexagons along the tube perimeter.

The interactions between hydrogen molecules are described by a Lennard-Jones potential

$$v_{LJ}(r) = 4\epsilon_{\text{H−H}}\left[\left(\frac{\sigma_{\text{H−H}}}{r}\right)^{12} - \left(\frac{\sigma_{\text{H−H}}}{r}\right)^{6}\right]$$

where r is the distance between the centres of mass of two hydrogen molecules, $\epsilon_{\text{H−H}} = 36.7$ K and $\sigma_{\text{H−H}} = 2.958$ Å. In addition to this pair potential, the hydrogen molecules interact by a quadrupole–quadrupole interaction which is taken into account by the Coulomb interactions of effective electric charges: two charges $q = 0.4829e$ located on the protons and one charge

$-2q$ at the centre of mass [22]. The interaction between hydrogen molecules and carbon atoms in the walls is also a Lennard-Jones potential with $\epsilon_{H-C} = 32.05$ K and $\sigma_{H-C} = 3.18$ Å. In graphite, the interaction between carbon atoms located in different basal planes is also described by $v_{LJ}(r)$; the short-ranged repulsive part of this interaction determines the minimal distance between the nanotube walls which is equal to $\sim$3.2–3.4 Å and is the minimal value of d.

Due to the small mass of hydrogen and the confinement of the molecules inside the nanotubes and the interstitial space between the tubes, the quantum effects are expected to contribute significantly to the adsorption process. These effects can be rigorously taken into account in simulations by the path-integral Monte Carlo method. But in the domain of temperature above 70 K considered here, the use of a Feynman–Hibbs effective potential which estimates the quantum effects exactly to the order of $\hbar^2$ is sufficient—the dimensionless parameter giving the magnitude of the quantum effects, $\hbar^2/(m_r \sigma_{H-H}^2 k_B T)$ (m_r: reduced mass of a pair of hydrogen molecules; k_B: Boltzmann constant) being equal to $\sim$0.07 at $T = 70$ K. The expression for the Feynman–Hibbs effective potential [23] is

$$v_{LJ}(r) = v_{LJ}(r) + \frac{\hbar^2}{24 m_r k_B T} \left(\frac{\partial^2 v_{LJ}(r)}{\partial r^2} + \frac{2}{r} \frac{\partial v_{LJ}(r)}{\partial r} \right).$$

The adsorption of hydrogen in the nanotube lattices described above has been computed by grand canonical Monte Carlo (GCMC) simulations (cf [17] for a description of the technical details of the simulations). This type of simulation reproduces the physical conditions of a thermodynamic equilibrium between the adsorbed gas and a gas in a large tank at a given temperature and definite chemical potential (or pressure).

The use of these nanotube lattices in a storage device for hydrogen is interesting only for an adequate choice of the values of D and d. These values must be of the order of the range of the attractive hydrogen–carbon interaction. Indeed, in a large domain of temperatures and at pressures lower than 20 MPa, at a distance of the order of σ_{H-C}, corresponding to the hydrogen–carbon interaction range, the hydrogen density close to a graphite basal plane is almost an order of magnitude larger than the bulk density. Beyond this distance it becomes rapidly equal to the bulk density. This result, established in [17, 18] for instance, by GCMC simulations of the adsorption of hydrogen in slits constituted of two parallel basal planes of graphite, provides the basis for the storage of hydrogen by physisorption. When D and d are of the order of σ_{H-C}, most of the volume inside and outside the nanotubes will be filled with hydrogen at a density much larger than the bulk density at the considered temperature and pressure. Then the amount of hydrogen stored by adsorption in the volume containing a nanotube adsorbent can be more important than that stored in the same volume without adsorbent filled with hydrogen at the bulk density.

The adsorption properties of two systems made up of 16 aligned nanotubes have been computed using the value $D = 13.3$ Å ($n = 17$) and the values $d = 3.4$ and 6 Å. For $d = 3.4$ Å, d has its minimal value and the parallel nanotubes are in a close-packed configuration of the two-dimensional triangular lattice. The nanotubes have a length of 34.08 Å and are enclosed in a parallelepipedic volume V with sides of 57.9, 34.08 and 66.8 Å respectively. The number of carbon atoms in V is $N_C = 8704$ and the density of the adsorbent is 1.31 g cm^{-3}. When d is equal to 6 Å, the sides of V are 66.8, 34.08 and 77.2 Å and the adsorbent density is 0.98 g cm^{-3}.

Similar arrangements of nanotubes have been studied in [17, 19, 20] where, at the temperatures of 293 and 77 K and pressures of $\sim$10 MPa, the values of D and d were determined to obtain a maximal amount of adsorbed hydrogen in V filled with the nanotubes compared to the amount of hydrogen which, in the same volume, would be stored by compression. In the domain of temperatures and pressures considered in this work the values $D = 13.3$ Å and $d = 6$ Å correspond to adsorption properties close to the best possible properties. By contrast,

Table 1. The adsorption isotherm at 293 K for the system of nanotubes of diameter $D = 13.3$ Å with $d = 3.4$ Å. First column: pressure P in megapascals; second column: bulk density ρ_b in g cm^{-3}; third column: density of adsorbed hydrogen for closed nanotubes ρ_c in g cm^{-3}; fourth column: density of adsorbed hydrogen for open nanotubes ρ_o in g cm^{-3}; fifth column: efficiency of adsorption versus compression; sixth column: weight percentage of H_2.

P	ρ_b	ρ_c	ρ_o	$(\rho_o - \rho_b)/\rho_b$	wt%
0.1	0.000 08	0.000 006	0.000 10	0.23	0.007
0.5	0.000 40	0.000 029	0.000 50	0.23	0.04
1.0	0.000 80	0.000 058	0.000 99	0.22	0.07
3.0	0.002 42	0.000 172	0.002 69	0.11	0.02
5.0	0.003 98	0.000 287	0.004 12	0.03	0.3
10.0	0.007 74	0.000 554	0.006 93	−0.10	0.5
15.0	0.011 28	0.000 818	0.009 11	−0.19	0.7
20.0	0.014 61	0.001 130	0.010 85	−0.25	0.8

Table 2. The adsorption isotherm at 293 K for the system of nanotubes of diameter $D = 13.3$ Å with $d = 6$ Å. First column: pressure P in megapascals; second column: bulk density ρ_b in g cm^{-3}; third column: density of adsorbed hydrogen for closed nanotubes ρ_c in g cm^{-3}; fourth column: density of adsorbed hydrogen for open nanotubes ρ_o in g cm^{-3}; fifth column: efficiency of adsorption versus compression; sixth column: weight percentage of H_2.

P	ρ_b	ρ_c	ρ_o	$(\rho_o - \rho_b)/\rho_b$	wt%
0.1	0.000 08	0.000 08	0.000 14	0.81	0.01
0.5	0.000 40	0.000 42	0.000 73	0.80	0.07
1.0	0.000 80	0.000 82	0.001 45	0.79	0.15
3.0	0.002 42	0.002 26	0.003 99	0.64	0.40
5.0	0.003 98	0.003 52	0.006 14	0.54	0.60
10.0	0.007 74	0.005 92	0.010 40	0.34	1.00
15.0	0.011 28	0.007 95	0.013 80	0.22	1.40
20.0	0.014 61	0.009 50	0.016 47	0.12	1.60

for $d = 3.4$ Å, the adsorption capacity of the nanotube material is low, but it is useful to notice that this value of the distance between nanotube walls could be that existing in the ropes of synthesized nanotubes. Comparison between the adsorption properties computed for the two values of d allows one to estimate the variation in the amount of hydrogen adsorbed in the interstitial space between nanotubes.

In the GCMC simulations, there are three possible MC steps: insertion, deletion and trial moves of molecules in V which are accepted in agreement with their grand canonical weighting. Clearly, it is possible to preclude the insertion of molecules inside the nanotubes and to compute the adsorption properties of porous materials made up of nanotubes with closed ends.

3. Results

The adsorption isotherm at 293 K has been computed from 0.1 to 20 MPa. This domain of pressures seems *a priori* appropriate to a movable storage of hydrogen using a tank of acceptable weight. Tables 1 and 2 give the results for systems with $d = 3.4$ and 6 Å, respectively. A comparison is made between the cases where the nanotubes are open and closed. When the nanotubes are closed, the adsorption is reduced by a factor of 10 if d has its minimal value of 3.4 Å and by a factor of 2 for d equal to 6 Å. These reductions of the adsorption capacity result from the decrease of the available surface for the adsorption and, in the case of d equal to 3.4 Å,
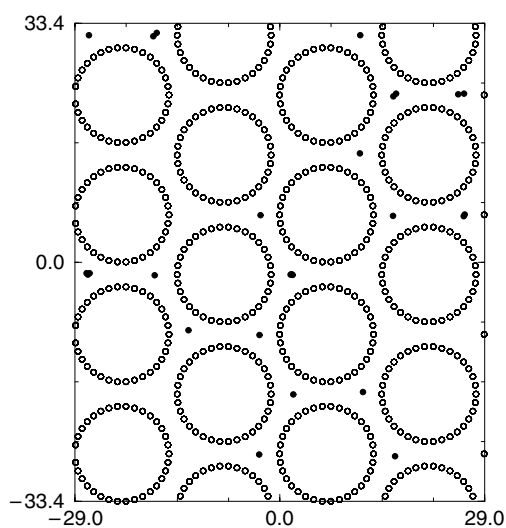
Figure 1. Projection on the xz-plane of adsorbed hydrogen molecules at 10 MPa and 293 K in a triangular lattice of closed nanotubes of diameter $D = 13.3$ Å with $d = 3.4$ Å. The open circles give the locations of nanotube walls, the black dots those of hydrogen molecules. The lengths of the sides of the simulation cell are in ångströms.

Figure 2. Projection on the xz-plane of adsorbed hydrogen molecules at 10 MPa and 293 K in a triangular lattice of open nanotubes of diameter $D = 13.3$ Å with $d = 6$ Å. The open circles give the locations of nanotube walls, the black dots those of hydrogen molecules. The lengths of the sides of the simulation cell are in ångströms.
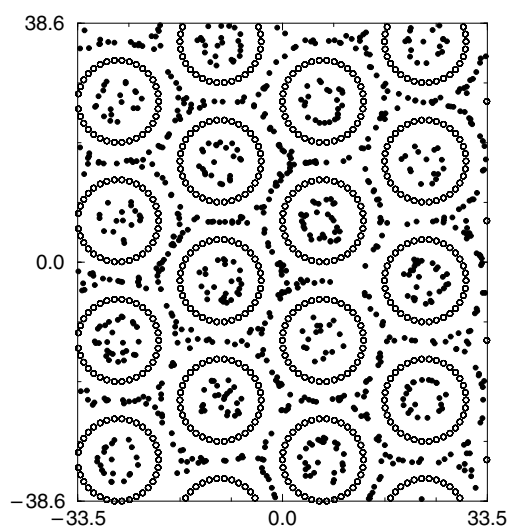
the small size of the interstitial space and external surface of the tubes where hydrogen can be adsorbed.

In figures 1 and 2 we present the projections of typical configurations of adsorbed hydrogen molecules on the xz-plane. Figure 1 shows clearly the small extension of the domain of V where the molecules can be inserted when the nanotubes have closed ends and are close packed;
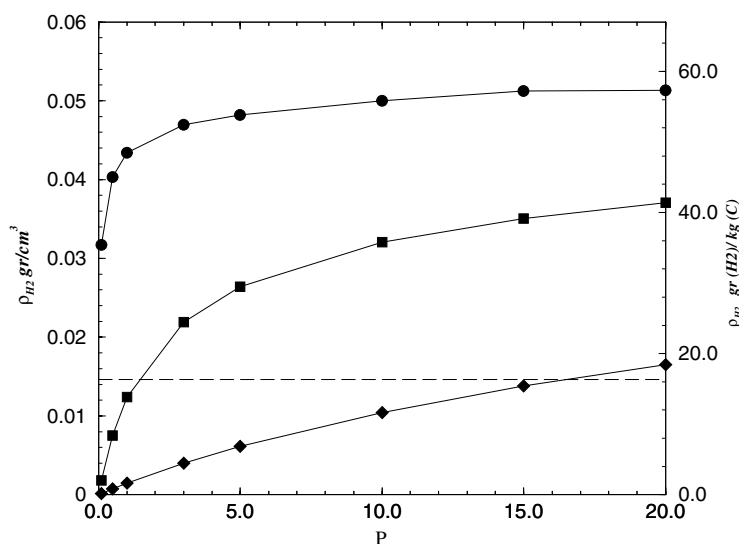
Figure 3. Adsorption isotherms between 0.1 MPa and 20 MPa: solid curve and filled circles: $T = 77$ K; solid curve and filled squares: $T = 150$ K; and solid curve and filled diamonds: $T = 293$ K. The hydrogen density is expressed in g cm^{-3} or g of hydrogen per kg of carbon; the pressure P is given in megapascals. The horizontal dashed line indicates a reference density for hydrogen storage chosen equal to the bulk density at 20 MPa and 293 K: 0.0144 g cm^{-3}.

figure 2 shows that, when $d = 6$ Å, the contribution of the interstitial space and external surface of nanotubes to the adsorption process is similar to that due to the internal volumes and surfaces of nanotubes. From these results, it seems possible to conclude that, in efficient storage of hydrogen, it is essential to use open carbon nanotubes in configurations where the minimal distance between the tube walls is ~6 Å (cf for a detailed discussion of the optimal value of this distance and tube diameter [17, 19, 20]).

When the pressure is less than 3 MPa and $d = 6$ Å in both cases where the nanotubes are closed and open, the amount of adsorbed hydrogen is larger than that which should be put into V by compression (cf table 2). For higher pressures, in the adsorbent made up of closed nanotubes, the amount of hydrogen stored by adsorption in V is smaller than that stored by means of compression.

The adsorption isotherms at 150 and 77 K have been computed from 0.1 to 20 MPa for the system of open nanotubes with $D = 13.3$ Å and $d = 6$ Å. Such a porous material has adsorption properties close to the optimum as mentioned above. The results are given in table 3 and plotted in figure 3. At $T = 150$ K and low pressures, the amount of hydrogen stored by adsorption is larger by a factor between 10 and 3 than that stored by compression; at 20 MPa this advantage of the adsorption over the compression remains and is of the order of 30%.

The amount of hydrogen stored by adsorption at 77 K is increased by a factor varying between 100 and 3 compared that stored by compression when the pressure varies from 0.1 to 3 MPa. For pressures higher than 15 MPa the storage by adsorption becomes disadvantageous compared to that by compression. At these pressures and this temperature, this effect results from the small difference between the bulk density and the density of hydrogen in the layers of adsorbed molecules. Since this difference between the two densities becomes marginal, the reduction of the volume available in V for the storage due to the presence of the nanotubes is not cancelled out by the adsorption.

Table 3. Adsorption isotherms at 77 and 150 K for the system of nanotubes of diameter $D = 13.3$ Å with $d = 6$ Å. First column: pressure P in megapascals; second column: bulk density ρ_b in g cm^{-3}; third column: density of adsorbed hydrogen for open nanotubes ρ_o in g cm^{-3}; fourth column: efficiency of adsorption versus compression; fifth column: weight percentage of H_2.

P	ρ_b	ρ_o	$(\rho_o - \rho_b)/\rho_b$	wt%
$T = 77$ K				
0.1	0.000 31	0.031 69	100.29	3.2
0.5	0.001 58	0.040 29	24.46	4.0
1.0	0.003 20	0.043 36	12.52	4.3
3.0	0.010 13	0.046 94	3.63	4.7
5.0	0.017 58	0.048 18	1.74	4.8
10.0	0.036 41	0.049 96	0.37	5.0
15.0	0.050 13	0.051 20	0.02	5.1
20.0	0.059 11	0.051 28	-0.13	5.2
$T = 150$ K				
0.1	0.000 16	0.001 80	10.26	0.2
0.5	0.000 79	0.007 51	8.40	0.7
1.0	0.001 60	0.012 36	6.71	1.2
3.0	0.004 74	0.021 90	3.61	2.2
5.0	0.007 82	0.026 40	2.37	2.6
10.0	0.015 13	0.032 03	1.11	3.2
15.0	0.021 79	0.035 02	0.60	3.5
20.0	0.027 82	0.037 05	0.33	3.7

Clearly, the results of the simulations depend on the choice of the interactions and the way one takes into account the quantum effects. These effects contribute to reducing the amount of adsorbed hydrogen by ~4% at 293 K and 20% at 77 K [19, 20]. Thus, it is important to remark that the present simulation data and those of [19, 20] are in excellent agreement with the simulation results obtained in [18]. In this latter publication, the intermolecular hydrogen interaction is described by the Silvera–Goldman pair potential [24] and the hydrogen–wall interaction inside and outside the nanotubes by averaged potentials derived from the hydrogen–carbon atom pair interaction. These averaged potentials, neglecting the corrugation of the wall surface, depend only on the distance between the axis of the nanotubes and the centre of mass of the hydrogen molecules. With this choice of interactions, the quantum effects are taken into account by the path-integral Monte Carlo method. The results obtained in [18], in particular the adsorption isotherms given in figure 5(a) at 77 K and figure 7(a) at 293 K in that paper, are similar to our simulation data presented in figure 3 and [20]. Taking into account the difference between the arrangements of nanotubes considered in this work, and in [20] and [18], at a pressure of 10 MPa it is possible to conclude that there is an adsorption capacity of 5–8 g of hydrogen per kilogram of nanotube adsorbent at 293 K and 20–45 g(H_2)/kg(C) at 77 K.

4. Discussion and conclusions

The efficiency of storage based on physisorption using porous materials made up of carbon nanotubes can be estimated from the simulation results. In order to determine this efficiency, the main characteristics of the adsorbent must be into account; these characteristics are the adsorption capacity and the density. The density of adsorbent models studied in this work is of the order of 1 g cm^{-3} and is similar of that of gasoline. This density is not strongly modified by the presence of adsorbed hydrogen, the mass of hydrogen molecules being small.

At $T = 293$ K, from the simulation results it is undoubtedly the case that an adsorbent made up of closed nanotubes in a close-packed configuration cannot constitute a favourable porous material for hydrogen storage. When the nanotubes are open, the amounts of adsorbed hydrogen for pressures lower than 10 MPa are larger than those which would be stored by compression in a volume identical to that containing the adsorbent. The quantity of adsorbed hydrogen can be increased by a factor of ~ 2 by an appropriate choice of the distance between the nanotube walls. But it is worth noticing that this distance does not seem a parameter that is easy to control in the processes used to synthesize nanotubes. For pressures larger than 10 MPa, when $d = 6$ Å, the weight (wt%) of adsorbed hydrogen expressed as a percentage of the weight of the adsorbent becomes larger than 1% and the storage by adsorption remains more efficient than that by compression.

For temperatures below room temperature, 'wt%' is of the order of 3–5. At 77 K and a pressure of 0.1 MPa the density of adsorbed hydrogen is 30.7 kg m^{-3} (~ 2 times the bulk density of hydrogen at 293 K and 20 MPa). At 150 K and 1 MPa, it is equal to 12.0 kg m^{-3} and, at 293 K and 10 MPa, to 10 kg m^{-3}. The corresponding bulk densities are 0.3, 1.5 and 7.5 kg m^{-3}, respectively.

Experimental confirmation of these theoretical estimates is not easy to obtain. In the synthesized samples, the nanotubes form ropes of parallel tubes which are separated by void spaces partly filled with impurities. To a large extent, these defects can be corrected by compaction and purification. But the nanotubes do not necessarily have equal diameters and open ends. In the domain of pressure and temperature considered in the simulations, numerous experiments have been realized to measure the hydrogen adsorption in the nanotubes. The results have been described in recent review articles [3–5, 8]. Examples of such measurements, performed at a temperature of 300 K and pressures from 0.04 to 12 MPa for single-walled nanotubes, are given in [9–15]; expressed in wt%, the measured adsorption capacities have values between 0.04 at 0.1 MPa [15] and 10 [9, 13] at 0.04 MPa. Capacities of ~ 4 at 12 MPa [10, 12], 1.5 at 0.1 MPa [11] and 0.35 at 0.1 MPa [14] have been obtained. In the case of multi-walled doped nanotubes for instance, an adsorption capacity of 14 wt% at 0.1 MPa has been reported [16].

The theoretical results given in tables 1 and 2 of ~ 0.01 at 0.1 MPa and ~ 1.0 at 15 MPa clearly differ from the experimental data. Since the experiments for the single-walled nanotubes do not agree and seem to have an accuracy that is difficult to assess, a credible estimation of the validity of the simulation data is unfortunately precluded. The theoretical results are in better agreement with the measurements realized on activated carbons [6–8]. For instance in [7], the measured adsorption equal to ~ 1.4 at 298 K and 12.5 MPa for activated carbon with a specific surface of ~ 3000 m^2 g^{-1} is close to the computed adsorption of the present adsorbent model of nanotubes.

On the basis of this theoretical study, in order to assess the applicability of the models of adsorbents studied to storage devices on board vehicles, the choice of a current movable storage of hydrogen as a reference is needed. A simple choice is that of the bottle of hydrogen of volume equal to 0.05–0.1 m^3, commonly used in research laboratories, having a weight of ~ 60–100 kg where hydrogen is stored at the pressure of ~ 20 MPa and room temperature, i.e. at a density of 14.4 kg m^{-3}. If this density is compared with those computed for the nanotube adsorbents given in table 2 and figure 3, it seems that storage by adsorption has marginal interest at 293 K, in particular for movable storage when the weight of the adsorbent is taken into account. At 77 K, adsorption is certainly an efficient means of storage since it is possible at 0.1 MPa to store ~ 30 kg m^{-3} of hydrogen, but this temperature seems excluded for a storage over a long period.

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