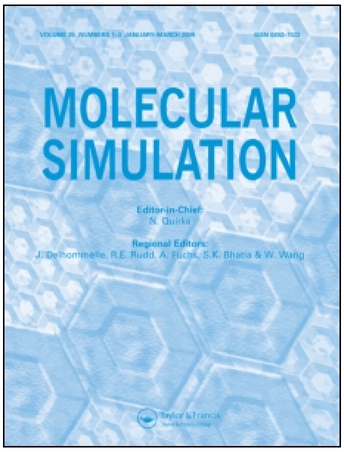

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QUANTUM CONTRIBUTION TO GAS ADSORPTION IN CARBON NANOTUBES

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Recently published Monte Carlo simulation studies have demonstrated that carbon nanotubes could be a new adsorbent material for the storage of gases such as hydrogen. This engineering application suitable for the use of hydrogen in fuel cells has motivated much experimental and theoretical work, including the present work. Using grand canonical Monte Carlo simulations, we have calculated the amount of hydrogen adsorbed in various arrangements of single-walled carbon nanotubes at high pressure and room temperature. For these thermodynamic states, we determined the importance of quantum effects on hydrogen adsorption. These quantum corrections were computed following a perturbative scheme already used, for instance, in simulation studies of phase diagrams of water, neon and methane. Taking into account the quantum corrections, we estimated, for each considered arrangement, the most favorable diameter and relative distance of the nanotubes for hydrogen adsorption.

Keywords: Hydrogen; adsorption; nanotube; simulation; quantum effects

1. INTRODUCTION

Since the discovery of carbon nanotubes by Iijima [1] in 1991, considerable activity has been devoted to the determination of the electronic properties [2] of microporous carbon materials. However gas physisorption in carbon nanotubes and new microporous materials made up of graphite nanofibers has also been the subject of many works. For instance, several studies and numerical simulation works have been carried out to estimate the density distribution or adsorption of molecular gases such as CH_4, N_2, Br_2 and H_2

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*Corresponding author. e-mail: dl@stat.th.u-psud.fr in single-walled carbon nanotubes, and their results have been confronted with the experimental data [3–6].

The molecules of simple gases adsorbed in microporous materials are confined in nanopores having a width of a few angströms. This confinement can modify the localization of the gas–liquid transition. Also, it can increase the value of quantum corrections which must be made on the results computed by using classical statistical mechanics if the thermal wave length of the adsorbed molecules is almost equal to the pore width. At low temperatures, these confinement effects are important [5]. At room temperature, which is largely above the critical temperature of the gas–liquid transitions of simple gases, they can change the classical estimate of the bulk thermodynamic properties of these gases by only a few percent but this change may be more appreciable on excess adsorption which is a typical surface property.

In a previous paper dealing with hydrogen adsorption in a material model made up of carbon nanotubes [3], we qualitatively estimated that the quantum effects would modify the amount of adsorbed gas by a few percent. In this work, by using grand canonical Monte Carlo simulations, we present a quantitative estimate of hydrogen adsorption in different arrangements of nanotubes taking into account the quantum contributions.

In Section 2, we describe the three different single-walled nanotube (SWNT) arrangements and the quantum correction methodology that we used. The Monte Carlo simulation procedure is briefly outlined. Section 3 is devoted to presenting the results of the simulations. A comparison is made between the calculated amount of gas adsorbed at room temperature and at a pressure of 10 MPa in these SWNT arrangements. In addition, we also determine the optimum arrangement of the carbon nanotubes, *i.e.*, giving the highest hydrogen adsorption. A short discussion concludes the article.

2. SWNT ARRANGEMENTS AND SIMULATION PROCEDURE

A nanotube is constructed by rolling up a rectangular piece of a basal plane of graphite in order to obtain a cylindrical single-walled carbon nanotube. In the simulations, we have considered different arrangements made up of lattices of nanotubes defined by two parameters: the diameter D of the nanotubes and the distance d between the walls of the nanotubes. The first and second arrangements are, respectively, a square and a hexagonal lattice of parallel nanotubes. In the third arrangement, the nanotubes are located within layers. In one layer, the axes of the nanotubes are equidistant and parallel to each other, but between two successive layers, the axes of the tubes are orthogonal to each other. These different arrangements are plotted in Figures 1–3.

We have computed hydrogen adsorption in these lattices by grand canonical Monte Carlo simulations, which are well adapted to the study of the adsorption process [6–9]. The simulation cells are parallelepipedic volumes containing 9 nanotubes in the case of the square lattice (Fig. 1) and 16 nanotubes in that of the hexagonal lattice (Fig. 2). For the latter type of arrangement, the simulation cell is a cubic volume filled by 16 nanotubes (Fig. 3). Simulations are performed by using cells with periodic boundary conditions in the x, y and z directions. It is worth mentioning that the use of periodic boundary conditions for the third arrangement imposes a constraint on the distance d which has to be chosen in agreement with the length L of the tubes.

The configurations of hydrogen molecules are generated by attempting to insert, to delete and to displace H_2 molecules in the simulation cell with an equal probability. Insertions of molecules are done at random in the volume

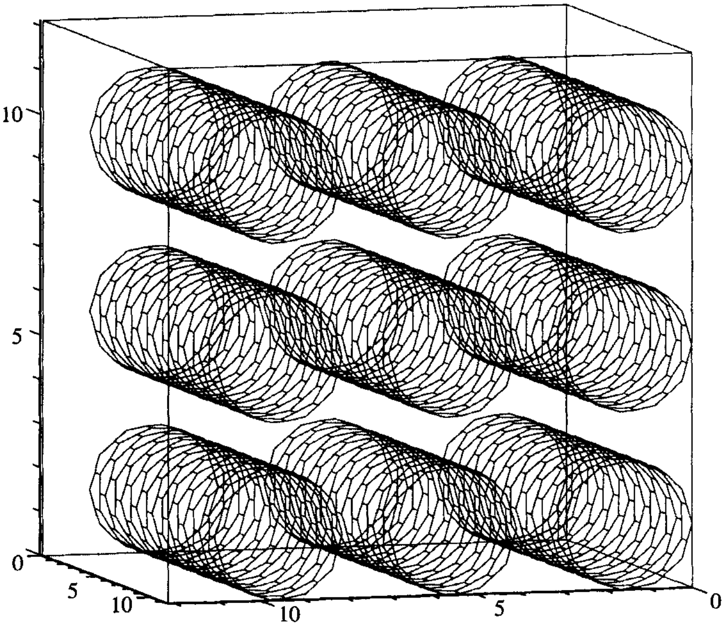

FIGURE 1 Simulation cell containing 9 carbon nanotubes disposed on the sites of a square lattice. The lengths of the simulation cell sides are $x = z = 12.141\,\sigma_{\mathrm{hh}} = 3.591\,\mathrm{nm}$ and $y = 11.521\,\sigma_{\mathrm{hh}} = 3.4070\,\mathrm{nm}$. The axes of the carbon nanotubes are parallel to the y axis.

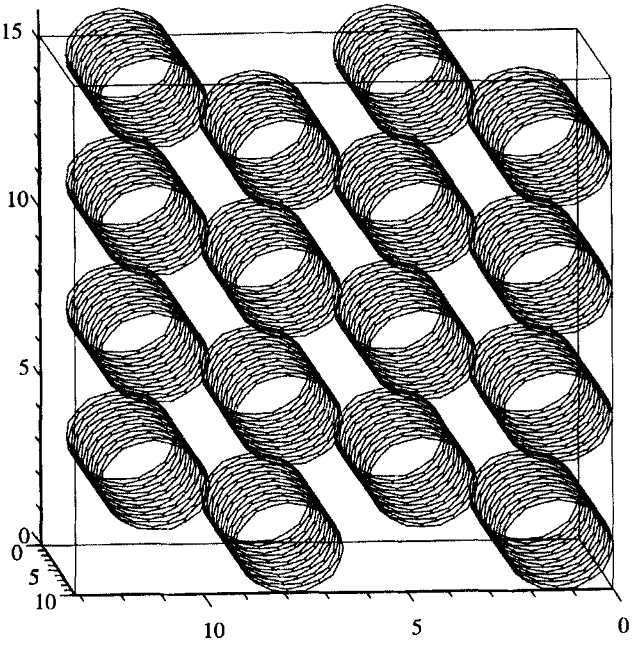

FIGURE 2 Simulation cell containing 16 carbon nanotubes disposed on the sites of a hexagonal lattice. The lengths of the simulation cell sides are $x = 13.10\sigma_{\mathrm{hh}} = 3.875\,\mathrm{nm}$, $y = 10.08\sigma_{\mathrm{hh}} = 2.981\,\mathrm{nm}$ and $z = 15.13\sigma_{\mathrm{hh}} = 4.475\,\mathrm{nm}$. The axes of the carbon nanotubes are parallel to the y axis.

of the cell and the deletions are carried out by choosing, at random, one of the molecules present in the simulation cell. Displacement (translation and rotation) is done by moving the position of a molecule at random in a small cubic volume. These *a priori* configurations of gas molecules are accepted according to the classical Metropolis sampling scheme [10, 9]. In a typical run, $0.8\ 10^6$ gas configurations are generated to obtain the equilibrium state of hydrogen molecules in the nanotubes, followed by $1.6\ 10^6$ configurations to estimate the average number of adsorbed hydrogen molecules $\bar{N}$ within a statistical error on the order of 1–2%.

For the thermodynamic state considered at temperature $T = 293\,\mathrm{K}$ and pressure $P = 10\,\mathrm{MPa}$, the thermal wavelength of hydrogen molecules $\Lambda = \mathrm{h}/\sqrt{2\pi m \mathrm{k} T}$ where h is the Planck constant, m the mass of the hydrogen molecule, and k the Boltzmann constant, is equal to 0.07 nm, and the typical distance σ between molecules is 0.2–0.3 nm. Since the value of the ratio between these two lengths is in the range of 0.1–0.2, it is legitimate to study the contribution of quantum effects to the hydrogen adsorption rates using a perturbative approach.

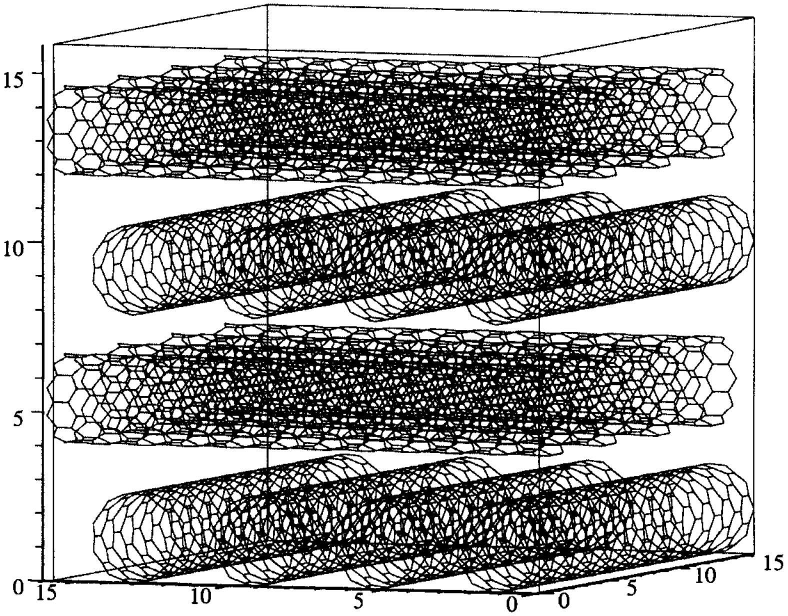

FIGURE 3 Simulation cell containing 16 carbon nanotubes arranged in a mixed configuration. Within one layer, the axes of the tubes are parallel to each other and between two successive layers, the axes of the tubes are orthogonal to each other. The lengths of the cubic simulation cell sides are $x = y = z = 15.84\sigma_{\mathrm{hh}} = 4.685\,\mathrm{nm}$.

A rigorous way to calculate the quantum contributions to thermodynamic properties of liquid systems is to use the path-integral method [11]. But in the case where the quantum contributions are *a priori* small, the Feynmann-Hibbs effective potential method [12] seems well suited. We quantitatively evaluate the quantum contributions by using this method, which corresponds to a systematic development of thermodynamic quantities in power of h^2. Indeed for low values of the ratio Λ/σ, this development according to [11 – 18] can be truncated to the first term. When the molecules interact by pair potentials, this approximation leads to a very simple way of taking into account the quantum corrections by adding to the pair interaction a term which is proportional to the Laplacian of the pair potential. Then, if the pair interaction between molecules is a Lennard-Jones (LJ) potential

$$V_{\mathrm{LJ}}(r) = 4\varepsilon_{\mathrm{LJ}}\left[\left(\frac{\sigma_{\mathrm{LJ}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{LJ}}}{r}\right)^{6}\right] \tag{1}$$

the Feynmann-Hibbs effective potential takes the following form

$$V_{\mathrm{LJ_{FH}}}(r) = V_{\mathrm{LJ}}(r) + \frac{\beta\hbar^2}{24\mu}\left(V''_{\mathrm{LJ}}(r) + \frac{2}{r}V'_{\mathrm{LJ}}(r)\right) \tag{2}$$

where $\beta = 1/\mathrm{k}T$ and μ is the reduced mass associated to the pair of atoms or molecules in interaction and the prime indicates a derivative with respect to r. In the literature, Feynmann-Hibbs quantum effective pair-potentials have been used successfully to compute, by Monte Carlo simulations, the quantum corrections to thermodynamics properties of fluids, for instance, for neon, methane [19, 20] and water [21].

We have considered quantum contributions from the intermolecular interactions between both gas–gas molecules and gas–carbon. In the simulations, the interactions between hydrogen molecules result from a LJ potential located at the center of mass of the molecules and a quadrupolar interaction. The hydrogen quadrupole is described by three charges: two charges q located on the protons and one charge $-2q$ located at the center of mass. The parameters of the LJ potential are equal to $\sigma_{\mathrm{hh}} = 0.2958\,\mathrm{nm}$ and $\varepsilon_{\mathrm{hh}} = 36.7\,\mathrm{K}$ and the value of q is $0.615\,10^{-26}$esu. The interaction between the hydrogen molecules and carbon atoms included in the nanotube walls is a LJ potential defined by $\sigma_{\mathrm{ch}} = 0.340\,\mathrm{nm}$ and $\varepsilon_{\mathrm{ch}} = 28.0\,\mathrm{K}$. From Eq. (2), it is straightforward to obtain the Feynmann-Hibbs potential associated with the LJ potential by considering that, for the H_2–H_2 interaction, $\mu = m/2$ and for the C–H_2 interaction $\mu = m$, since we assume that the carbon atoms are rigidly linked together inside the nanotube walls.

We use σ_{hh} and $\varepsilon_{\mathrm{hh}}$ as units of length and energy to express the chemical potential, temperature and density. The computations are made at a chemical potential equal to -2.7 and $T^* = 7.988$ (293 K), giving a pressure of 10 MPa, corresponding to a hydrogen bulk density equal to $\rho_b^* = 0.06$. In the simulations, the Lennard-Jones interactions were truncated at a distance $r_C = 5.2\,\sigma_{\mathrm{hh}}$, because, beyond this distance, the LJ potential is smaller than $2 \times 10^{-4}\varepsilon_{\mathrm{hh}}$. The contribution of the quadrupole–quadrupole interaction between hydrogen molecules to thermodynamic properties is small; thus the quantum corrections arising from this multipole interaction have not been considered.

3. RESULTS AND DISCUSSION

We have determined the hydrogen adsorption for different values of D and d in the three lattices of nanotubes. The results are given in Tables I, II

TABLE I Hydrogen adsorption data at 293 K and 10 MPa in carbon nanotubes disposed on a square lattice (*cf.* Fig. 1). The first column gives carbon nanotube diameters D (nm) and the second gives the distance d (nm) between the tubes. The third column gives the average number $\bar{N}$ of gas molecules in the cell. N_c is the average number of gas molecules that should be present in the volume V^* of the simulation cell without the nanotubes. g_a (%) gives the relative efficiency of gas adsorption compared to gas compression. $\bar{N}_C$ is the average number of gas molecules adsorbed without quantum corrections. C_o (%) is the relative difference between $\bar{N}_C$ and $\bar{N}$ and is an estimate of the quantum effects on the gas adsorption

D	d	$\bar{N}$	N_c	$g_a\%$	V^*	$\bar{N}_C$	$C_o\%$
0.704	0.34	84.5	77.6	9	1293.142	90.1	6
1.018	0.34	144.4	130.6	10	2184.686	152.3	5
1.174	0.34	184.6	163.1	13	2717.621	194.7	5
1.331	0.34	224.8	198.5	13	3308.663	234.5	4
1.644	0.34	316.2	279.9	13	4665.072	329.6	4
1.957	0.34	422.4	375.2	13	6253.913	437.0	3
0.704	0.6	164.7	121.0	36	2016.978		
1.018	0.6	245.3	186.1	32	3101.503		
1.174	0.6	293.6	223.8	31	3730.926		
1.331	0.6	344.4	265.1	30	4418.458		
1.644	0.6	453.7	358.1	27	5967.846		
1.957	0.6	579.1	464.9	24	7749.665		
0.704	0.7	189.4	140.3	35	2338.039	197.9	4
1.018	0.7	277.8	209.8	32	3496.786	288.1	4
1.174	0.7	327.9	249.8	31	4163.321	342.0	4
1.331	0.7	380.8	293.3	30	4887.964	391.6	3
1.644	0.7	497.4	390.7	27	6511.575	511.3	3
1.957	0.7	627.5	502.1	25	8367.617	644.7	3
0.704	0.9	225.5	183.1	23	3051.267		
1.018	0.9	320.7	261.5	23	4358.459		
1.174	0.9	375.2	305.9	23	5099.217		
1.331	0.9	431.8	353.8	22	5898.083		
1.644	0.9	556.0	460.2	21	7670.138		
1.957	0.9	692.8	580.5	19	9674.626		

and III. The average numbers of hydrogen molecules $\bar{N}$ in the volumes V^* of the simulation cells have been computed with and without quantum corrections. From the values of $\bar{N}$, V^* and $\rho_b^* = 0.06$ we can estimate the excess number N_e of H_2 molecules adsorbed in the simulation cell due to the presence of the nanotubes. Since the average number of H_2 molecules which should be inside the volume V^* in the absence of the nanotubes is $N_c = \rho_b^* V^*$, N_e is equal to $\bar{N} - N_c$. We characterize the adsorption properties of a specific nanotube arrangement by g_a defined by $g_a = 100\,(\bar{N} - N_c)/N_c$.

Before analysing the simulation results, it is important to remark that, σ_{ch} being equal to 0.32 nm, the $C-H_2$ short range repulsive interaction imposes that the smallest distance r_s between a H_2 molecule and a nanotube wall is equal to 0.30–0.32 nm. Then a nanotube with a diameter D smaller than 0.60–0.65 nm cannot be filled by H_2 molecules. This excluded volume effect is reinforced by the contribution to $V_{\mathrm{LJ_{FH}}}$ of the pair potential Laplacian

TABLE II Same as Table I for the case where carbon nanotubes are disposed on a hexagonal lattice (*cf.* Fig. 2)

D	d	$\bar{N}$	N_c	$g_a\%$	V^*	$\bar{N}_C$	$C_o\%$
0.704	0.34	82.7	119.5	~ 0	1990.922		
1.018	0.34	153.6	201.8	~ 0	3363.545		
1.174	0.34	208.9	251.0	~ 0	4184.051		
1.331	0.34	272.2	305.6	~ 0	5094.021		
1.644	0.34	434.8	430.9	~ 0	7182.349		
1.957	0.34	598.9	577.7	~ 0	9628.529		
0.704	0.6	264.7	186.3	42	3105.341		
1.018	0.6	393.1	286.5	37	4775.074		
1.174	0.6	468.7	344.6	36	5744.136		
1.331	0.6	550.5	408.2	35	6802.661		
1.644	0.6	727.7	551.3	32	9188.099		
1.957	0.6	925.6	715.8	29	11931.390		
0.704	0.7	308.4	215.9	43	3599.647	319.6	4
1.018	0.7	450.6	323.0	39	5383.654	469.7	4
1.174	0.7	531.6	384.6	38	6409.852	554.8	4
1.331	0.7	618.8	451.5	37	7525.514	640.1	3
1.644	0.7	801.5	601.5	33	10025.225	833.3	4
1.957	0.7	1012.7	772.9	31	12882.789	1040.6	3
0.704	0.9	362.3	281.8	29	4697.733		
1.018	0.9	508.7	402.6	26	6710.287		
1.174	0.9	598.1	471.0	27	7850.758		
1.331	0.9	689.0	544.8	26	9080.693		
1.644	0.9	881.7	708.5	24	11808.951		
1.957	0.9	1096.5	893.7	23	14895.062		

TABLE III Same as Table I for the case where carbon nanotubes are disposed on a mixed lattice (*cf.* Fig. 3)

D	d	$\bar{N}$	N_c	$g_a\%$	V^*	$\bar{N}_C$	$C_o\%$
0.704	0.7	539.9	393.7	37	6562.424	558.7	3
1.018	0.7	972.9	734.1	32	12234.725	1006.9	3
1.174	0.7	1175.6	880.5	33	14675.099	1219.4	4
1.331	0.7	1596.5	1229.3	30	20487.518	1645.9	3

which increases faster than the pair potential for distances smaller than σ_{ch}. Furthermore at room temperature, as it was shown in Ref. [3], the domain of the distances near the nanotube walls where the attractive interaction between walls and H_2 molecules makes the hydrogen local density larger than the bulk density at 10 MPa, extends from r_s to $\sim r_s+\sigma_{\mathrm{hh}}$. From these remarks, we conclude that, in the central region of the nanotubes, the local density should be equal to the bulk density when D is larger than 1.3 nm ($\simeq 2(r_s+\sigma_{\mathrm{hh}})$). Outside the nanotubes, the local density also will be equal to the bulk density in the regions of the volume V more distant from a nanotube wall than $r_s+\sigma_{\mathrm{hh}}$.

These qualitative remarks are confirmed, at a large extent, by the results of the simulations obtained for the three nanotube lattices. In these simulations, we have considered that d, the minimal approach distance between the nanotube walls, could not be smaller than 0.34 nm which is the distance between the basal planes in a graphite crystal. In Table I, the number of adsorbed H_2 molecules are reported for the square lattice. For this lattice when $d = 0.34$ and D is larger than 1.1 – 1.3 nm, the value of g_a which characterizes the excess of H_2 molecules in V^*, stays stationary. This result is in agreement with the hypothesis that the central part of the tubes and the region outside the tubes far from the walls are filled with molecules at the bulk density. For the lattices with d equal to 0.6 nm or 0.7 nm, the simulations data are almost similar and show that g_a decreases when D increases. Since g_a would be negative if the free volume outside and inside the tubes was filled by hydrogen gas at the bulk density, this behavior is explained by the fact that for increasing D, an increasing part of V is filled by H_2 at the bulk density leading to a reduction of g_a which is not compensated by the gas adsorption on the larger surface of the nanotube walls. For the lattice with d equal to 0.9 nm, the variation of g_a with the increase of D is similar to that found for the lattices with $d = 0.6$ nm or 0.7 nm, but the values of g_a are smaller. This result could be expected because, a large increase of the nanotube spacing leads necessary to a large increase of the volume filled by the bulk density.

For the hexagonal lattice (*cf.* Tab. II), the variation of g_a is similar to that obtained for the square lattice. We remark that for $d = 0.34$ nm, g_a is around zero because the nanotube arrangement being very compact, the volume excluded to hydrogen molecules by the nanotube walls is an important part of V. At $d = 0.9$ nm for all values of D, g_a is smaller than in the cases where d is equal to 0.6 nm and 0.7 nm. From the values of g_a computed for the square and hexagonal lattices, it appeared that the most favorable values of d and D for the H_2 adsorption are 0.6 – 0.7 nm and 0.7 – 1.0 nm, respectively. The results obtained for the third arrangement presented in Table III, have shown that an important change in the relative position of the nanotubes did not seem to modify this conclusion.

From the comparison made in Tables I – III with the results of simulation performed in neglecting the quantum corrections, it is clear that these corrections for given values of d and D decrease the amount of adsorbed H_2 molecules. This decrease of $\bar{N}$ is weak and does not exceed 5%. This latter value confirms our previous qualitative estimates [3] and shows that, at the considered thermodynamic state, the main consequence induced by the use of the effective $V_{\mathrm{LJ}_{\mathrm{FH}}}$ potentials is to increase the steepness and range of the pair repulsive interactions at short distance limiting slightly the accessible volume to the gas in the simulation cell.

4. CONCLUSION

We have determined the amount of adsorbed hydrogen in different material models made up of single-walled nanotubes and we have quantitatively estimated the importance of the quantum effects on this process. These computations have been performed at temperature of 293 K and pressure of 10 MPa by assuming that the interactions between H_2 molecules and carbon atoms are LJ potentials. Such potentials are believed to be an acceptable representation of these interactions, but they could be insufficient in the case where the walls of nanotubes would have not been obtained by rolling up perfect basal graphite planes and would present many defects.

The maximum of adsorption seems reached when the nanotubes have diameters of 0.7 – 1 nm and are arranged in a hexagonal lattice and distant at least from 0.6 – 0.7 nm. However, we remark that the differences on the maximum adsorption for the considered lattices are not very large. This result seems to indicate that the adsorption properties of these material models are determined mainly by the values of the diameter and spacing of the nanotubes and are largely independent from the choice of the global arrangement of the tubes. A final remark is that the porous material made up of SW carbon nanotubes seems to have a large adsorption ability which exceeds by a factor four that of the best activated carbons [22].

References

[1] Iijima, S. (1991). "Helical microtubules of graphitic carbon", *Nature*, **354**, 56.

[2] Zhu, H.-Y., Klein, D. J., Schmalz, T. G., Rubio, A. and March, N. H. (1998). "Geometric boundary effects on the electronic properties of the finite carbon nanotubes", *J. Phys. Chem. Solids*, **59**, 417.

[3] Darkrim, F. and Levesque, D. (1998). "Monte Carlo simulation of hydrogen adsorption in single-walled carbon nanotubes", *J. Chem. Phys.*, **109**, 4981.

[4] Rzepka, M., Lamp, P. and de la Casa Lillo, M. A. (1999). "Physisorption of hydrogen on microporous carbon and carbon nanotubes", *J. Phys. Chem. B*, **102**, 10894.

[5] Wang, Q. and Johnson, J. K. (1999). "Molecular simulation of hydrogen adsorption in single-walled carbon nanotubes and idealized carbon slit pores", *J. Chem. Phys.*, **110**, 577.

[6] Wang, Q. and Johnson, J. K. (1999). "Computer simulations of hydrogen adsorption on graphite nanofibers", *J. Phys. Chem. B*, **103**, 277.

[7] Vermesse, J. and Levesque, D. (1992). *Mol. Phys.*, **77**, 837.

[8] Vermesse, J. and Levesque, D. (1994). *J. Chem. Phys.*, **101**, 9063.

[9] Parsonage, N. G. and Nicholson, D. (1982). Academic Press, London.

[10] Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H. and Teller, E. (1953). "Equation of state calculation by fast computing machines", *J. Chem. Phys.*, **21**, 1087.

[11] Feynmann, R. P. and Hibbs, A. (1965). "*Quantum mechanics and path-integrals*", New-York – McGraw-Hill.

[12] Feynmann, R. P. (1972). New-York – Benjamin.

[13] Wigner, E. (1932). "On the quantum correction for thermodynamic equilibrium", *Phys. Rev.*, **40**, 749.

[14] Hansen, J. P. and Weis, J. J. (1969). "Quantum corrections to the coexistense curve of neon near the triple point", *Phys. Rev.*, **188**, 314.

[15] Kirkwood, J. G. (1933). "Quantum statistics of almost classical assemblies", *Phys. Rev.*, **44**, 31.

[16] Barocchi, F., Neumann, M. and Zoppi, M. (1987). "Almost classical static properties of a Lennard-Jones many-body system", *Phys. Rev. A*, **36**, 2440.

[17] Berne, B. J. (1986). "On the simulation of quantum systems: path integral methods", *Ann. Rev. Phys. Chem.*, **37**, 401.

[18] Neumann, M. and Zoppi, M. (1989). "Asymptotic expansions and effective potentials for almost classical N-body systems", *Phys. Rev. A*, **40**, 4572.

[19] Sesé, L. M. (1992). "A quantum Monte Carlo study of liquid Lennard-Jones methane, path-integral and effective potentials", *Mol. Phys.*, **76**, 1335.

[20] Sesé, L. M. (1995). "Feynman-Hibbs potentials and path integrals for quantum Lennard-Jones systems: theory and Monte Carlo simulations", *Mol. Phys.*, **85**, 931.

[21] Guillot, B. and Guissani, Y. (1998). "Quantum effects in simulated water by the Feynman-Hibbs approach", *J. Chem. Phys.*, **108**, 10162.

[22] Darkrim, F., Vermesse, J., Malbrunot, P. and Levesque, D. (1999). "Monte Carlo simulations of N_2 and H_2 physisorption at high pressure and room temperature. Comparison with experiments", *J. Chem. Phys.*, **110**, 4710.