



## Adsorption of polar and non-polar fluids in carbon nanotube bundles: Computer simulation and experimental studies

A. Wongkoblap<sup>a,1</sup>, D.D. Do<sup>a,\*</sup>, K. Wang<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, University of Queensland, St. Lucia, Queensland 4072, Australia

<sup>b</sup> Division of Chemical and Biomolecular Engineering, Nanyang Technological University, Singapore 637459

### ARTICLE INFO

#### Article history:

Received 8 September 2008

Accepted 19 November 2008

Available online 24 November 2008

#### Keywords:

Adsorption

Carbon nanotube

GCMC

Non-polar fluid

Polar fluid

Tube bundles

### ABSTRACT

The effects of adsorbate on the adsorption in a bundle of carbon nanotubes are investigated to explore the preferential adsorption over various adsorption sites: inside the tube, in the cusp interstices and in the square interstices outside the tubes. This is carried out with the Grand Canonical Monte Carlo simulation and the simulation results are tested against the experimental results of bundles of single wall carbon nanotubes (SWCN). With regard to adsorbate, we choose argon and nitrogen to represent simple fluids and water to represent strong associating fluids with strong orientation interaction. The preferential adsorption of argon and nitrogen depends on the tube size. For tube size smaller than 10.8 Å, adsorption inside the tube is preferred because the solid–fluid potential is greatest in the tube interiors. While for larger tubes adsorption occurs initially in the small cusp interstices between the tubes, and as adsorption is progressed adsorption occurs inside the tube as well as the larger square interstices. At higher pressures capillary condensation occurs in the square interstices. For water, however, the adsorption mechanism is different. Its adsorption occurs dominantly inside the tube, irrespective of the tube size. This is due to the requirement of appropriate geometry to allow hydrogen bonding among water molecules to occur. The small cusp interstices do not provide proper space for clusters of hydrogen bonded waters, while the larger square interstices are too large and hence the solid–fluid potential is not strong enough to induce adsorption unless the partial pressure is sufficiently high. Finally the model of these fluids and carbon nanotube is tested with the experimental data of a commercial SWCN, and the simulation results are in agreement with the data.

© 2008 Elsevier Inc. All rights reserved.

### 1. Introduction

Single walled carbon nanotubes (SWCNs) consists of a single graphene sheet rolled into a unique tubular shaped with a very narrow tube size in one dimensional nano-scale [1–3]. SWCNs have been increasingly used in many applications, for example methane [4] and hydrogen [5–7] storages, sensor technology and medical technology [8] since the discovery of carbon nanotube by Iijima in 1991 [9]. It is reported in the literature [7] that SWCNs could act as metals or as semiconductors [10,11], and as such chemical reaction could occur inside the nanotubes [12], and the adsorption of NO<sub>2</sub>, O<sub>2</sub> and NH<sub>3</sub> [13,14] in carbon nanotubes is also affected by their electronic properties which depend on the carbon atoms arrangement. SWCNs can stick to each other and form bundles due to the strong van der Waals interactions [15]. As a result ad-

sorption of fluids can occur outside SWCNs at the cusp interstices where the fluid–solid interaction potentials are enhanced to give the deepest potential minimum [3]. The characterization of the porosity of SWCNs and the adsorption mechanism of fluids in nanotube bundles are important for all applications. To characterize solids, argon and nitrogen are often used at their respective boiling points; however argon is preferred due to its spherical shape and its zero dipole and quadrupole. Therefore its adsorption on surface is non-specific compared to nitrogen. Water vapor could affect the performance of SWCNs in the purification or separation of gaseous mixtures. Therefore, it is important to understand the adsorption of water in nanotube bundles and this can be applied to study the adsorption of mixture involving water.

Several experimental works have been carried out on the adsorption of nitrogen [3,15–19], argon [19–21] and water [1,22] in carbon nanotubes. To elucidate the adsorption mechanism of these fluids in carbon nanotubes, molecular simulation (Monte Carlo and Molecular Dynamics) have been used [3,7,15,21–27]. For these methods to give correct results, the choice of fluid and solid model used in the simulation method is important. The isolated single nanotubes have been commonly used in many simulations; but

\* Corresponding author. Fax: +61 7 3365 2789.

E-mail address: d.d.do@uq.edu.au (D.D. Do).

<sup>1</sup> Present address: School of Chemical Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand 30000.

this simplistic model does not truly represent experimental carbon nanotubes because these tubes are usually found in tangled or partly aligned bundles [23]. In this study the carbon nanotubes bundle consisted of seven SWCNs, one at the centre and the others arranged at the vertices of a hexagon is used as a solid model while the fluid model used ranges from the simple one of a spherical molecule for argon to the complex one of a tetrahedral structure for water molecule. Argon and nitrogen are used as non-polar fluids while water represents polar fluids with strong association (hydrogen bonding) to see whether the adsorption of non-polar fluid in nanotubes is different from that of polar fluid. Simulation studies of nitrogen adsorption in carbon nanotubes were based on a spherical model [15,23], but in the confinement of nanotubes its shape is important and it should be modeled as a diatomic molecule [28]. To test the importance of molecular shape, both potential models (spherical and diatomic) are used in our computer simulation.

For water, two classes of potential models have been used in the literature. One is the point charge models such as SPC/E model [29], while the other is the square well site models such as the Primitive model (PM) [30–33] and the Muller et al. [34,35] models. The point charge model involves long-range Coulombic forces which require a large simulation system size in order to minimize the cut-off errors induced due to the effect of simulating a finite system [34] and the greatly increased computation time [36], while the Muller et al. model can mimic the association without the need for large simulation system and computation time [37]. This model uses the off-centre square well interactions to describe bonding sites [38] and increases the energy well depth for unlike sites to form the hydrogen bonding which accounts for the electrostatic and attractive forces [34]. The quantum and bond flexibility effects are not taken into account because they are insignificant [38]. The molecular parameters are evaluated by using Wertheim's TPT1 theory and fitted to thermodynamic properties such as the gas-liquid coexistence properties of bulk water at 298 K; Gibbs ensemble and isothermal-isobaric simulations for this water model yielded the vapor pressure and coexisting densities of gas and liquid phases which agreed well with the experiment [34,35]. The Muller et al.'s model can describe adsorption behavior of water in slit pore [34,35,37,39] and cylindrical pore [27] equally well, when compared against models with partial charges such as SPC/E [7,26,36,37,40]. The comparison between the simulation results of this model for a functionalized graphitic and the experimental data of commercial activated carbon has been reported in the literature [35,39,41], and agreement is found to be satisfactory.

This study focuses on using homogeneous nanotubes bundles to investigate the adsorption of fluid in carbon nanotubes. The adsorption isotherms and isosteric heats of argon at 87.3 K, nitrogen at 77 K and water at 298.15 K are obtained by using a Grand Canonical Monte Carlo (GCMC) simulation. The effects of nanotube diameter ( $D$ ) and the spacing between the nearest neighbor SWCNs ( $s$ ) on the adsorption of these fluids will be investigated to determine any differences in their adsorption mechanisms.

## 2. Methodology

### 2.1. Fluid model

In this study, argon is used as a model species for simple Lennard-Jones (LJ) fluids [42] while nitrogen is treated as a simple spherical molecule with a single LJ centre and a rigid non-spherical model with partial charges to simulate quadrupole. The non-spherical model has two interaction sites located at the centre of nitrogen atoms separated by 1.1 Å, a positive charge at the centre of the molecule and two negative charges at the centre of

**Table 1**  
Molecular parameters used in this study.

Fluid	$\sigma_{ff}$ (Å)	$\varepsilon_{ff}/k$ (K)	$r_{NN}$ (Å)	$r_{OH}$ (Å)	$\sigma_{HB}$ (Å)	$\varepsilon_{HB}/k$ (K)
Ar	3.405	119.8	–	–	–	–
N <sub>2</sub> (1 LJ site)	3.615	101.5	–	–	–	–
N <sub>2</sub> (2 LJ sites)	3.320	36.4	1.1	–	–	–
H <sub>2</sub> O	3.060	90.0	–	1.2852	0.612	3800

Note. N: nitrogen atom; O: oxygen atom; H: hydrogen atom; HB: hydrogen bonding.

nitrogen atoms. The electrostatic value of the positive charge of  $12.98 \times 10^{-20}$  C and that of the negative charge of  $-6.49 \times 10^{-20}$  C are used [43–45]. The Muller et al. water potential model [34] used in this study models a water molecule with one dispersive site (oxygen atom) at the centre of a tetrahedron and four square-well (SW) associating sites positioned at the vertices of the tetrahedron. These four sites represent two hydrogen atoms and two lone pairs of electrons. The molecular parameters used in this study are listed in Table 1, where  $\varepsilon_{ff}$  and  $\sigma_{ff}$  are the energy well depth and the collision diameter of fluid, respectively and  $k$  is the Boltzmann's constant,  $r_{NN}$  is the separation distance between nitrogen atoms,  $r_{OH}$  is the distance between a SW site and the oxygen atom,  $\varepsilon_{HB}$  is the potential well depth for unlike associating sites (a lone pair of electrons of one water molecule and a hydrogen atom of another water molecule) to form a hydrogen bond while that for the like associating sites interaction is zero, and  $\sigma_{HB}$  is the collision diameter of two unlike associating sites. A cut-off radius in the calculation of interaction energy of five times the collision diameter of fluid ( $5\sigma_{ff}$ ) is used in this study. The interaction energy between fluids ( $\varphi_{ff}$ ) is calculated using the Lennard-Jones 12-6 equation:

$$\varphi_{ff}(r) = 4\varepsilon_{ff} \left[ \left( \frac{\sigma_{ff}}{r} \right)^{12} - \left( \frac{\sigma_{ff}}{r} \right)^6 \right], \quad (1)$$

where  $r$  is the separation distance. Beside the interaction between two LJ sites, the interaction between two charges for nitrogen molecule and that between two SW sites for water molecule should be taken into account. In the case of water, if A represents a hydrogen atom on one water molecule and B is a lone pair of electrons on another water molecule, the interaction potential energy between A and B to form a hydrogen bond is [30–32]

$$\varphi_{HB}(r_{AB}) = \begin{cases} -\varepsilon_{HB}, & r_{AB} < \sigma_{HB} \\ 0, & \text{otherwise,} \end{cases} \quad (2)$$

where  $r_{AB}$  is the distance between A and B. In this study, the long-range interactions are not taken into account.

In the case of nitrogen modeled as the 2-centre-LJ molecule with 3 point charges, the interaction between two charges, each of which is on different molecule, takes the form of a Coulomb law of electrostatic interaction.

$$\varphi_{q^a q^b}(r^{ab}) = \frac{1}{4\pi\varepsilon_0} \frac{q^a q^b}{r^{ab}}, \quad (3)$$

where  $\varepsilon_0$  is the permittivity of free space,  $r^{ab}$  is the distance between two charges  $a$  and  $b$ .

### 2.2. Solid model

The solid model used in this study is the carbon-based adsorbents whose pores are cylindrical in shape. This model has seven tubes arranged in a hexagonal pattern. Fig. 1 shows a schematic diagram of a cross section of bundles of Single Wall Carbon Nanotubes (SWCN) and the minimum image convention of the model. Each cylindrical pore consists of one graphene wall and its diameter ( $D$ ) is that of a ring passing through the centres of the carbon layer. The distance between two carbon atoms in a graphene layer

Download English Version:

<https://daneshyari.com/en/article/611129>

Download Persian Version:

<https://daneshyari.com/article/611129>

[Daneshyari.com](https://daneshyari.com)