Carbon Dioxide Transport in Carbon Nanopores

Dimitrios Mantzalis, Nikolaos Asproulis, Dimitris Drikakis
Fluid Mechanics and Computational Science Department, Cranfield University, UK
E-mail: n.asproulis@cranfield.ac.uk

Abstract. In the present study atomistic simulations are employed for investigating the CO$_2$ transport properties through pores that are of slit, cylindrical and scroll configuration. We aim to investigate any possible differences in the adsorption process among the three different geometries focusing on the adsorption type that occurs along with pore filling and pore emptying mechanisms. Carbon-slit pores are of widths between 0.8 and 2.0 nm. The simulated Single-Walled Carbon Nanotubes (SWNTs) are of 1.08 and 2.17 nm ((8,8) and (16,16) respectively) while for the Carbon Nanoscrolls (CNSs) the inner diameter corresponds to a (6,6) SWNT with an intralayer distance of 0.4 to 1.0 nm.

1. Introduction
Climate change due to global warming is one of the main challenges that modern world faces. The development of novel techniques and methods able to capture and separate green house emissions and primarily carbon dioxide from fossil fuels, atmosphere and natural gas has attracted the industrial and scientific interests[1, 2]. Nanotechnology and more specifically carbon nanostructures as a relative new scientific field can provide solutions based on materials designed to offer superior properties, compared to traditional filtering approaches, in terms of selectivity, capacity and flux rates[3, 4].

Over the last two decades a number of studies, both experimental and computational, have been carried out aiming to investigate the transport properties of gases through carbon nanostructures such as carbon nanotubes (CNTs), carbon slit pore (CSP) and carbon nanoscrolls (CNS) [5, 6, 7, 8]. These different forms of nanostructures have been utilised for developing novel carbon capture devices able to operate under a wide range of conditions. Carbon Nanoscrolls (CNS), firstly fabricated in 2003 [9], are novel carbon based materials initially reported to be promising for H$_2$ storage [10]. CNS display a spiral form and are schematically obtained by wrapping a graphite sheet in a helical formation.

Computational and experimental evidence show that both gases and liquids can be transported through carbon nanopores, such as CNTs, orders of magnitude faster compared to ordinary microporous materials such as zeolites [11]. Their nearly frictionless walls combined with their very small pore size offer increased transport efficiency making them ideal adsorbents [3, 4].

Although great amount of studies that have been devoted in confined liquids within CNTs and CSPs, pure or functionalized, little attention has been attracted to CNSs and to comparative studies between the three carbon allotropes[12, 13, 8]. In the present work, we draw our attention in the CO$_2$ transport and adsorption properties of three carbon allotropes and specifically on carbon nanotubes, carbon slit pores and carbon nanoscrolls. Specifically, we perform a direct...
comparison among the three carbon allotropes in terms of \( CO_2 \) capture and we aim to investigate any possible differences in the adsorption process among the three different geometries focusing in the adsorption type that occurs along with pore filling and pore emptying mechanisms. The present article is structured as follows: Section 2 outlines the simulation methodology and the models employed, Section 3 provides the results of the study along with the corresponding discussion and Section 4 the main conclusions together with future work.

2. Simulation Method

The nanotubes considered in the present work are of type armchair while their carbon atoms, \( C^* \), are modeled as Lennard-Jones spheres, holding them in their equilibrium crystallographic positions during the simulations. In practice, carbon nanotubes, mainly those with large pores, are flexible materials; however the choice of frozen curvature reduces the computational cost. Several studies have shown that the deviations observed into these two approaches can be initially ignored; self-diffusion computed for simple fluids in rigid tubes has been found to predict higher values compared with cases that flexibility is involved in the computations [14, 8]. This effect are negligible in narrower pores in cases where the confined liquid reaches high densities. The choice of frozen curvature in combination with the fixed relevant motion between \( C^* \) atoms, reduces the computational cost compared with a flexible model. However several studies have shown that the disagreements between the two techniques can be ignored in first place. In the present work, the nanotubes have been assumed to be rigid as in case of the narrow (8,8) SWNT, the \( C^* \) vibrations are not expected to affect the diffusion mechanism of carbon dioxide molecules bearing in mind the small overestimation of self-diffusion as stated by Skoulidas et al. [15]. The two indices used for describing a SWNT, such as (8,8), characterize the way that the graphene sheet is wrapped and the CNTs diameter is given by:

\[
d = \frac{a}{\pi} \sqrt{(n^2 + nm + m^2)}
\]

where \( a = 0.246 \text{nm} \).

The microcanonical ensemble (NVE) [16] has been used for the integration of the equations of motion, where the number of molecules in the system (\( N \)), the volume of the simulations box (\( V \)) and the system’s total energy (\( E \)) are kept constant. The simulations have been carried out with LAMMPS [17] with the integration time step is \( \delta t = 0.5 \text{ fs} \) for avoid large fluctuations of the total energy and the temperature of the system. The system has been equilibrated for 200 – 600 ps, period that has been disregarded for the further calculations according to the charge of the CNTs. To ensure that the temperature fluctuations will not considerably deviate from the set value of 300 \( K \), a temperature rescaling has been employed during the equilibration period every 1000 time steps.

The carbon dioxide molecules are simulated through the 3-site model suggested by Murthy et al. [18]. Previous computational studies regarding the interaction potential between carbon nanostructures and \( CO_2 \) have shown that 3-site models offer more realistic representations with respect to 1-site models and the differences between the available linear models in the literature is negligible[19]. A Lennard Jones (LJ) potential is employed to mimic the Van der Waals interactions with the \( \varepsilon \) and \( \sigma \) parameters being \( \varepsilon_{CC}/k_B = 29.0 \text{ K} \), \( \varepsilon_{OO}/k_B = 83.1 \text{ K} \), \( \sigma_{CC} = 2.785 \text{ Å} \) and \( \sigma_{OO} = 3.014 \text{ Å} \) and with \( CO_2 \) mass being equal with 44.010 \( g/mol \)[18]. At carbon and oxygen sites partial charges have been introduced with \( q_C = 0.5957 \) and \( q_O = q_C/2 \), respectively, and mixed LJ parameters are computed based on the Lorentz-Berthelot rule. For the bonds and angles of carbon dioxide molecules the SHAKE algorithm [17] is utilised with the equilibrium length and angular values being reset at every time step to their equilibrium figures \( l_{CO_2} = 1.16 \text{ Å} \) and \( C-O-C = 180^\circ \) respectively. The interaction LJ parameters used between the nanopores and the carbon dioxide are \( \varepsilon_{C^*}/k_B = 28.0068 \text{ K} \) and \( \sigma_{C^*} = 3.4 \text{ Å} \) [20], where \( C^* \) corresponds to carbon atom of the nanopores.
3. Results and Discussion

Figure 1 shows for pressure $P = 5 \text{ bar}$ the layering formation close to the nanopores surface for a (8,8) CNT, a CNS with interlayer distance 7.0 Å and a CSP with the graphene layers being 8.1 Å away from each other. The volume close to the nanopore in each case is divided to bins parallel to the nanostructure graphitic walls with characteristic $\text{CO}_2$ structures being formed in the proximity of the nanopores surface independently to the shape of the pore. The number and the relative strength of the layers formed near depend upon a number of parameters such as diameter in case of CNTs, interlayer distances, partial charges and gas-structure interactions.

![Figure 1](image1.png)

(a) CNT  
(b) CNS  
(c) CSP

**Figure 1.** Projections of $\text{CO}_2$ distributions (a) (8,8) CNT (b) CNS − 7.0 Å (c) CSP − 8.1 Å

Figure 2 shows the number of $\text{CO}_2$ molecules adsorbed per carbon atom $C^*$ as a function of time for all the three CNTs ((8,8), (12,12) and (16,16) respectively) that have been simulated. It is noticed that for the three cases as time evolves the number of carbon dioxide molecules adsorbed both in the internal and external surface of the CNT approaches a mean value with an additional fluctuating component that varies with the radius of the CNT and gets higher values for the (16, 16) case. The smaller adsorbing capacity is equal to 0.045 $\text{CO}_2$ molecules per carbon atom $C^*$ and is noticed for 5.37 Å radius. For the (8,8) nanotube its radius compared to the
van der Waals one is 1.58 time higher and therefore does not allow the formation of a secondary layer within its internal volume explaining the reduced adsorbing performance. As the CNT diameter increases to 8.10 Å, for the (12,12) CNT, the non-dimensional adsorption obtains its maximum mean value 0.068; however the standard deviation of the fluctuating component is slightly increased compared to the previous case mainly due to the smaller binding energy[21]. As the larger nanotubes such as (16,16) (see Fig. 2) the surface-to-volume ratio of the CNT increases leading to smaller number of carbon dioxide molecules adsorbed per C∗[14].

![Graph showing CO₂ adsorption over time for different CNTs](image)

**Figure 2.** CO₂ molecules adsorbed per carbon atom C∗ as a function of time for (8,8), (12,12) and (16,16) CNTs

Figure 3 shows the number of CO₂ molecules adsorbed per carbon atom C∗ as a function of time for CNSs with 5.6Å, 7.0Å and 8.3Å layering distances respectively. Compared the CNT case larger adsorbing values are reported mainly due to the higher surface-to-volume ratio that the nanoscrolls present compared to the CNTs and the lower energy needed for a molecule to enter the scrolls internal volume. As the interlayer distance of the nanoscroll increases from 5.6Å to 7.0Å the average carbon dioxide adsorption decreases and then as it further increases to 8.3Å it settles back to its initial values. It can be noticed that as the interlayer increases the surface-to-volume ratio and the standard deviation of the fluctuating component decreases showing a preference for smaller binding energies.

Figure 4, similarly to Figs. 2 and 3, demonstrates the number of carbon dioxide molecules adsorbed as function of time for the three CSPs employed in the present study. The main points regarding the adsorbing capacity of the slit pores with respect to time and interlayer distances are similar to previous cases. A main difference though that can be identified is the almost zero adsorption of the slit pore with 5.3Å distance between the graphene sheets. For this interlayer distance the carbon dioxide molecules cannot enter in the interlayer region and the binding energy of those that lay in the proximity of the outer surface is small explaining therefore the poor adsorption performance.

Figures 5 and 6 demonstrate the gravimetric and volumetric carbon dioxide uptake of the different nanopores simulated as a function of pressure. As pressure increases the number of
Figure 3. \( \text{CO}_2 \) molecules adsorbed per carbon atom \( C^* \) as a function of time for CNSs with 5.6Å, 7.0Å and 8.3Å layering distances respectively.

Figure 4. \( \text{CO}_2 \) molecules adsorbed per carbon atom \( C^* \) as a function of time for CSPs with graphene sheets being 5.3Å, 8.1Å and 10.8Å apart respectively.

\( \text{CO}_2 \) increases leading to a more closely packed arrangements of carbon dioxide molecules and consequently to increased numbers near or within the nanopores. CSP arrangements in both cases (Fig. 5(c) and 6(c)) present lower adsorption capacity among the structures examined.
and as pressure increases it looks to approach their saturation point much faster as the slope of the graph continuously decreases. Furthermore it has to be noticed that the binding energies values reported for slit pores are lower compared to nanotubes and nanoscrolls making CSPs less attractive structures for gas storage and filtering.

The volumetric and gravimetric uptake CNTs and CNSs looks to scale almost linearly with pressure and, apart from CNS case, and we do not notice any saturation indications. For the carbon nanotubes the (8, 8) is the one that presents higher uptake values for both measures since its radius allows only one very strong internal carbon dioxide layer leading at the same time to higher adsorption energies as has been reported in previous studies in the literature [14]. In the volumetric uptake as the diameter of nanotube increases the surface-to-volume ratio decreases as well contributing to lower adsorbing levels. The same applies to CNSs with larger interlayer distance as shown in Fig. 6(b) as the interlayer distance increases from 5.6Å to 8.0Å the uptake decreases in a non-linear fashion.

Figure 5. Gravimetric CO₂ uptake for (a) a carbon nanotube (b) carbon nanoscroll (c) carbon slit pore at 300 K

4. Conclusions
In conclusion, in the present paper the effect of the nanopore structure in terms of carbon dioxide uptake is examined for a number of pressures. Three types of nanopore are considered:
nanotubes, nanoscrolls and slit pores with equivalent geometrical characteristics and in all cases the formation of carbon dioxide layers in the vicinity of the pores graphitic walls is noticed. The layers formed close to the nanopores wall vary based on the structure and its properties, such as radius or interlayer distance, showing that the geometry of the structure has be cautiously selected for optimum performance. In terms of uptake the lower values have been reported for slip pores whereas for nanotubes and nanoscrolls higher figures have been obtained for both volumetric and gravimetric uptake. A clear selection between CNTs and CNSs cannot be easily performed and additional studies have to be carried out for exploring the performance of these nanopores for pressure and temperature conditions. Towards this direction maybe Grand Canonical Monte Carlo simulations have to be employed for faster scanning of the entire phase-space.

5. References
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Figure 6. Volumetric $CO_2$ uptake for (a) a carbon nanotube (b) carbon nanoscroll (c) carbon slit pore at 300 K
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