Confinement of CO₂ inside carbon nanotubes

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Abstract. We propose a preliminary study based on molecular dynamics calculations to investigate the adsorption of pure CO₂ on flexible single-walled carbon nanotubes (SWCNTs) of different sizes. The adsorption capacities of SWCNTs were simulated and the effect of chirality and diameter of SWCNTs was assessed, to check them as sizable carbon structured materials suitable for CO₂ confinement and storage. The potential energy surfaces, describing the intermolecular interactions involving CO₂-SWCNT and CO₂-CO₂ pairs, have been described specifically by adopting the improved Lennard-Jones model potential. The intramolecular interactions within the SWCNT were considered explicitly since they are responsible for out-of-plane movements of carbon atoms and the flexibility of nanotubes. These well-formulated potentials are well capable of defining CO₂ confinement through physisorption and guarantee a quantitative description and realistic results for the dynamics of the interactions. The flexible SWCNTs can adsorb up to 35 wt% at 273 K, a property that makes them potentially versatile materials competitive with other carbon-derived adsorbents to cope with CO₂ gas emission.

1 Introduction

The high concentration of CO₂ in the atmosphere leads to many serious problems, such as environmental pollution, increasing the apparition frequency of poisonous blue-green algae and, most importantly, it is seen as a possible cause for rising of global temperature potentially leading to catastrophic climate change effects [1]. Recent scientific reports have revealed that CO₂ emission to the atmosphere has significantly risen in the last decades [2]. Large-scale human activities for fulfilling their various needs, involving manufacture materials processing (steel, iron, cement, etc.) or energy production, majorly contribute to this increasing trend [3]. Consequently, it is urgent to implement strategies to turn the evolution trend, keeping the CO₂ at the current level or even reducing the CO₂ concentration in the atmosphere [4]. In order to achieve this goal, we can consider two main approaches, either by capturing CO₂ molecules in the open air or in sites where CO₂ molecules are generated. The latter is usually chosen as the most efficient, effective and energetically feasible than the first [5]. However, the main constraint is that the flue gas is commonly in a form of mixture composed from water, carbon dioxide, oxygen and nitrogen molecules [6]. Therefore, a method which can provide selective CO₂ capture is highly desired. The selectivity of various methods such as those involving

solid adsorbents, liquid absorbents, and hybrid materials composed of liquid absorbents and solid adsorbents have been evaluated to capture CO₂ from flue gas [7–9]. Among those methods, CO₂ capture using solid adsorbents attracted global attention in the last few years [10, 11]. This method offers major advantages, for instance for its simplicity and the relatively cheaper implementation on existing power plants [3, 5]. Moreover, solid adsorbents have minimum chemical risks that usually arise with the use of traditional amine solvents (e.g. equipment corrosion, solvent evaporation, chemical stability, and unpleasant smells) [12].

The range of options of applicable solid adsorbents for CO₂ capture and separation is vast, only materials with high selectivity and high gravimetric uptake is the best suited option. Permeability also plays an important role, in which it corresponds to diffusion of gas inside the materials to produce effective gas adsorption [13]. In order to attain high gravimetric value, a material should have large surface area (adsorption sites) in combination with its lightweight structure. Large surface area is normally achieved by introducing intrinsic pores on a nanometer scale, thus obtaining so-called nanoporous materials. A range of nanoporous materials for CO₂ capture and separation have been reported, for instance, zeolitic imidazolate frameworks (ZIFs) and zeolites [14, 15], porous polymer networks (PPNs) or covalent organic polymers/frameworks (COPs/COFs) [16–18], metal-organic frameworks (MOFs) [19, 20], and nanoporous carbons [21–23]. In particular, carbon-based materials exhibit desirable physicochemical prop-

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erties (e.g. chemically inert, relatively high hydrophobicity and thermally stable). Moreover, they are composed from lightweight carbon atoms producing low density and stable structures [24]. In contrast, MOFs and zeolites-based materials despite showing good gas uptake as well as good selectivity and permeability, they are made up by heavy elements in their structures. Therefore, the net of gravimetric densities reported in term of wt% are commonly quite low. Moreover, MOFs are generally known to have low structural stability at certain conditions (e.g. high temperature, acidic environment) and they are less resistant to the nucleophilic attack of water molecules [3]. Unfortunately, post-combustion flue gas commonly bear water vapour at a relatively high temperature.

Nanoporous carbon materials can be found in the form of 1, 2, 3-dimensional structures. Each of these structures has its own pros and cons, so that a certain structure is commonly suitable for a certain application. A class of carbon-based materials that is investigated in this work is the well-known Carbon NanoTubes (CNTs), in particular the single walled CNTs (SWCNTs). SWCNTs are one-dimensional carbon structures that are equipped with an intrinsic cavity inside the tubular-like structures. The large available volume within SWCNTs promises the possibility for CO₂ confinement. With their robust and light-weight structures, it is beneficial to exploit SWCNTs capacity as CO₂ capture and storage materials suitable to be used in movable/mobile platforms. One characteristic of these SWCNTs is that they have different physicochemical properties depending on their chirality and diameter. The phenomenon of adsorption dynamics and the corresponding mechanism as the effect of diameter and chirality are still an important line of research [25]. One of these adsorption mechanisms is generally involving physical adsorptions, which depends mainly on the electrostatic interactions and the weak (but not less important) van der Waals interactions. This physisorptions process occurs rapidly and perhaps through unimolecular (single-molecule) process. Accordingly, a preliminary study using a computational modelling and running simulations is crucial to gain atomistic perception into the interactions [26–28].

Molecular dynamics (MD) simulations performed by using accurate intramolecular and intermolecular potentials are a strength tool to describe particular dynamical adsorption system and to get practical energetic details at a given temperature [29]. Although some molecular dynamics simulations have also been implemented to study the CO₂ adsorption on CNTs [30, 31], in this work the emphasis is on the accuracy of the intermolecular and intramolecular potentials. These potentials have been modelled and specifically formulated for CO₂ and CNTs by adopting an improved representation of the van der Waals contribution and by applying flexibility to CNTs structures. In comparison with this work, three charge-site of CO₂ models, rigid CNTs and the conventional Lennard-Jones potential were used in reported literatures [30, 31].

This report is arranged as the following. The illustration and details of the computational methods, including the formulation of different components composing the force fields, are presented in the next section. The MD simulations details are given in the Sect. 3 along with discussion of the results.

2 Computational methods

The total potential energy function, V_{total} , adopted to calculate the total interaction energy for CO₂ molecules and the SWCNT is formulated as a sum of two separable terms. Of these, one, denoted as V_{SWCNT} , accounts for the SWCNT intramolecular potential energy, and the other one, denoted as V_{intermol} , accounts for the intermolecular potential energy of the SWCNT–CO₂ and CO₂–CO₂ interacting pairs:

$$V_{\text{total}} = V_{\text{SWCNT}} + V_{\text{intermol}} \quad (1)$$

where

$$V_{\text{intermol}} = \sum_{i=1}^l \sum_{j=1}^n V_{C_i-(CO_2)_j} + \sum_{j=1}^{n-1} \sum_{k>j}^n V_{(CO_2)_j-(CO_2)_k} \quad (2)$$

In the above equation n is the amount of CO₂ molecules, while l represents the number of carbon atoms in the SWCNT.

2.1 Bonding interactions in SWCNT

In the course of MD simulations, the carbon nanostructures were allowed to vibrate to reproduce the consequent out-of-plane movements of SWCNT surfaces by adopting intramolecular potential reported in Ref [32]. The corresponding intramolecular potential (V_{SWCNT} in Eq. 1) of flexible SWCNT is computed as a sum of potential energy terms depending on bond lengths, bending angles and dihedral angles, as follows:

$$V_{\text{SWCNT}} = \sum U(r_{ij}) + \sum U(\theta_{ijk}) + \sum U(\phi_{ijkl}) \quad (3)$$

where the r_{ij} 's are the interparticle distances, the θ_{ijk} 's are the bending angles between triples of consecutive atoms i, j, k and ϕ_{ijkl} is the dihedral angle defined by a given set of four consecutive C atoms of the SWCNT; summation, running over atom indices, is intended to avoid redundant terms. The stretching potential $U(r_{ij})$ of a C–C interatomic bond in the SWCNT is framed as a Morse potential function:

$$U(r_{ij}) = E_0 \{ [1 - \exp(-k(r_{ij} - r_0))]^2 - 1 \} \quad (4)$$

where r_{ij} represents the interatomic radius between C atom i and j , E_0 is the well depth (114.4569 kcal mol^{−1} Å^{−2}), r_0 is the equilibrium distance (1.418 Å) and $k = 2.1867$ Å^{−1} is connected to the bond force constant.

Valence angle potential ($U(\theta_{jik})$) terms for the bond bending of nanotubes are formulated by harmonic cosine functions:

$$U(\theta_{jik}) = \frac{k}{2}(\cos(\theta_{jik}) - (\cos(\theta_0)))^2 \quad (5)$$

θ_{jik} represents the angle between C_j - C_i - C_k atoms, θ_0 is the equilibrium value (120°), while k is the force constant ($134.5 \text{ kcal mol}^{-1}$). A triple cosine function is used for the dihedral angle potentials ($U(\phi_{ijkl})$), describing the interaction arising from torsional forces:

$$U(\phi_{ijkl}) = \frac{1}{2}A_1(1 + \cos(\phi_{ijkl})) + \frac{1}{2}A_2(1 - \cos(2\phi_{ijkl})) + \frac{1}{2}A_3(1 + \cos(3\phi_{ijkl})) \quad (6)$$

where the parameter values are $A_1 = A_3 = 0$ and $A_2 = 6.0096 \text{ kcal mol}^{-1}$.

2.2 CO₂-SWCNT and CO₂-CO₂ interactions

Describing correctly the intermolecular potential ($V_{intermol}$) is essential in order to obtain accurate results in a MD simulation. In this study, the intermolecular forces of interest are those occurring between CO₂ molecules and between CO₂ and SWCNT. Electrostatic and non-electrostatic contributions are the two components that composed the intermolecular interaction energy. The electrostatic part can be simply determined by using the Coulomb law. On the other hand, the non-electrostatic contribution is evaluated by taking into consideration the pairwise induction and dispersion long range attractive interactions and short range repulsion, which add up resulting in the van der Waals forces, which are expressed for each interacting pairs using the so-called Improved Lennard-Jones (ILJ) pairwise function [33–35]:

$$V_{ILJ}(r) = \varepsilon \left[\frac{m}{n(r) - m} \left(\frac{r_0}{r} \right)^{n(r)} - \frac{n(r)}{n(r) - m} \left(\frac{r_0}{r} \right)^m \right] \quad (7)$$

In the Eq. 7, the parameters ε and r_0 correspond to the well depth and the equilibrium position of the given interacting pair, respectively. m has the value of 1 for ion-ion, 4 for ion-neutral and 6 for neutral-neutral pairs interactions. The left term of the Eq. 7 (inside big bracket) depicts the repulsion as a function of the distance r , while the right term in the equation performs the long-range attraction. To modulate the strength of the attraction and the decline of the repulsion in Eq. 7, the $n(r)$ term is defined as follows:

$$n(r) = \beta + 4.0 \left(\frac{r}{r_0} \right)^2 \quad (8)$$

where β is a parameter for modulating the hardness of the interacting pair [36,37]. All of the ILJ parameters that were implemented in this study were fine-

tuned and benchmarked in comparison with *ab initio* calculations as reported in Ref. [38,39]. The ILJ function is much more accurate than the classical Lennard-Jones (LJ) potential function routinely used in Force-Fields for the prediction of static and dynamical properties of systems. In particular, ILJ systematically corrects the excessive long range attraction and short range repulsion of LJ potential, where the long and short-range deviations can impact adsorption dynamics. These advantages of using ILJ over conventional LJ potential have been reported in literatures [33–45].

3 Molecular dynamics (MD) simulations

The MD simulations were realized within the NVE microcanonical and NVT canonical ensembles enforcing periodic boundary conditions with a rectangular cuboid box. In our MD simulations, starting from a given initial configuration, each system considered in the MD simulations was equilibrated for 0.3 ns. The production period was recorded for another 9.7 ns, leading to a total of 10 ns simulation time with a time step value set at 2.5×10^{-4} ps. The cutoff radius for the electrostatic and non-electrostatic ILJ terms were set to 19 Å to speed up the computation of the force field. The data collected during the equilibration period were excluded from the statistical analysis of the simulations for which the DL_POLY package [46] was used. Energy contributions, CO₂ distributions, gravimetric densities of CO₂ as a function of simulation time and the corresponding average values have been subsequently analyzed. The VMD software [47] has been used to construct the SWCNT structures. After the SWCNT structures were obtained, for each simulation systems, 100 CO₂ molecules were randomly added around the nanotubes surfaces at a distance of 5–8 Å. This corresponds to a bulk gas density value of about 89.10 g L^{-1} . The CO₂ model reported in Ref. [38] was adopted with its point charge distributions corresponds to a five charge-site as shown in Fig. 1. This five charge-site model is more superior in treating quadrupole moment of CO₂ than the widely used three charge-site models adopted in Refs. [30,31].

We report detailed MD simulation results for 100 CO₂ molecules on three types of zigzag open-ended SWCNTs (i.e. (5,0), (10,0) and (15,0)) with different chiralities to examine their CO₂ confinement capabilities. All of SWCNTs compose five unit cells, thus for (5,0), (10,0), and (15,0) structures, each contain 100, 200 and 300 carbon atoms, respectively (Fig. 2). The SWCNTs were modelled as non-rigid structures during MD simulations. The flexibility of adsorbent materials through its molecular vibrations has been demonstrated altering its uptake capacity of adsorbing molecules such as hydrogen, nitrogen and methane [32,48]. Most importantly, treating SWCNT as a flexible structure provides more realistic representation of adsorbent and yields simulation data closer to those of the more precise results.

Fig. 1 Structural representation of CO_2 molecule using five charge-site model. Q is a point charge placed on the C–O bond of CO_2 molecule. The charge values are reported in a.u

Fig. 2 SWCNTs used in the MD simulations. Upper part: (15,0) structure; middle part: (10,0) structure; lower part: (5,0) structure

A CO_2 molecule must be within the SWCNTs cavity or at a maximum distance of 7 Å from the surface of the SWCNTs, in order to decide whether the CO_2 molecule is physically adsorbed. These criteria are following indications obtained in the previous works [39, 49, 50] and from the initial evaluation of radial den-

Fig. 3 Density of CO_2 inside the simulation box as function of radius from CNT surface at 273 K

sity plots (Fig. 3). Figure 3 justifies that radius of 7 Å from CNT surface has covered the full peaks of CO_2 , therefore it can be considered as adsorption region. The radial density is an analogue of z-density in which the z axis is replaced by radius from CNT surface. In order to analyze the effect of various MD parameters to the distribution of CO_2 molecules, firstly, we determined the amount of adsorbed molecules at the exohedral and endohedral sites of the carbon nanotubes. The effect of temperature on this distribution was investigated by setting three initial temperatures at 273, 300 and 353 K. Meanwhile, to investigate the dependence of the CO_2 distribution on the diameter of the SWCNTs, we made molecular simulations with different diameters. The next step was analyzing the radial distribution function to determine the composition of the repulsive and attractive interactions that exists between CO_2 molecules and the SWCNT. The results for each SWCNTs are presented in Table 1.

Table 1 records the number of adsorbed CO_2 molecules in exohedral ($N_{\text{CO}_2,\text{out}}$) and endohedral ($N_{\text{CO}_2,\text{in}}$) sites simulated at NVE ensemble. The temperatures reported in Table 1 indicate the average value at the end of MD simulations. As expected, due to the adsorption phenomenon, the average temperature is lower

Table 1 MD parameters and the amount of adsorbed CO_2 molecules at NVE ensemble

SWCNT	d (Å)	N_e	T (K)	$N_{\text{CO}_2,\text{in}}$	$N_{\text{CO}_2,\text{out}}$	$C_{\text{CO}_2,\text{in}}$	$C_{\text{CO}_2,\text{out}}$
(5,0)	3.914	100	253.1	0 ± 0	27 ± 4	0 ± 0	0.11 ± 0.02
			266.8	0 ± 0	26 ± 4	0 ± 0	0.11 ± 0.02
			302.8	0 ± 0	22 ± 4	0 ± 0	0.09 ± 0.02
(10,0)	7.828	200	253.2	4 ± 0	43 ± 5	0.01 ± 0	0.09 ± 0.01
			277.8	4 ± 0	36 ± 7	0.01 ± 0	0.07 ± 0.01
			305.8	4 ± 0	34 ± 4	0.01 ± 0	0.07 ± 0.01
(15,0)	11.743	300	262.1	16 ± 1	48 ± 5	0.02 ± 0	0.07 ± 0.01
			285.6	15 ± 1	43 ± 8	0.02 ± 0	0.06 ± 0.01
			326.8	14 ± 1	37 ± 4	0.02 ± 0	0.05 ± 0.01

$N_{\text{CO}_2,\text{out}}$ and $N_{\text{CO}_2,\text{in}}$ indicate the number of CO_2 molecules adsorbed outside and inside of SWCNTs, while $C_{\text{CO}_2,\text{in}}$ and $C_{\text{CO}_2,\text{out}}$ are the number of adsorbed CO_2 per unit of surface area (molecules $\text{\AA}^{-2}$) inside and outside SWCNT, respectively

Fig. 4 The amount of confined CO₂ inside the SWCNTs at 300 K as a function of time. The (5,0) structure has 0 value since its diameter is too small for CO₂ confinement

than the initial temperature for each system. We have noticed that not all of the CO₂ molecules were physically adsorbed. Table 1 shows that the amount of CO₂ at the exohedral and endohedral sites rises with the increasing of nanotube diameter. This trend is due to the fact that the available volume at endohedral and exohedral sites enlarges as the SWCNTs diameter increases. We also report the amount of confined CO₂ in a unit of mg g⁻¹ (Fig. 4), by considering that CO₂ molecule is confined if it is adsorbed in an endohedral site of the SWCNT. Figure 4 shows that the (15,0) structure can confine up to 184 mg CO₂ for 1 g of adsorbent. This value is equivalent to 15.54 wt(%), which can fairly be considered a quite large gas uptake value. On the contrary, the (5,0) structure is not suitable for CO₂ confinement since its effective diameter is smaller than the kinetic diameter of CO₂ (see Fig. 2). Therefore, in this small pore, repulsion forces are dominant with respect to the attractive ones. These findings are consistent with a study reported by Goler et al. [51] which suggest that adsorptions of molecules on graphene surfaces are controlled by the local curvature. The preferential adsorption sites are reported in the area where its curvature is maximally convex. The surface curvature inside of (5,0) structure is highly concave, thus CO₂ adsorptions are energetically unfavored. Meanwhile in the outside of (5,0) structure, having high convexity level, it adsorbs high CO₂ uptake in term of molecules per unit of surface area as reported in Table 1. It is clear that by increasing the diameter of SWCNT, the degree of surface convexity inside the SWCNT also increases. Therefore, CO₂ confinement inside SWCNT is directly proportional with the diameter of carbon nanotubes (Table 1).

Figure 5 shows the molecular configuration after 10 ns of simulation for the (10,0) system as an illustrative example of the equilibrium. It can be seen in Fig. 5 that the endohedral site can be occupied by CO₂ to accommodate molecular confinement. In addition, the exohedral site also exhibits adsorption properties with

Fig. 5 Snapshot of final configuration of the (10,0) structure with 100 CO₂ molecules at 300 K

a much higher CO₂ uptake (Table 1 and Fig. 5). Therefore, in order to provide a more quantitative ground, the total storage capacity (SC) of SWCNTs was evaluated at every step of the trajectory by calculating gravimetric density, wt(%), as the following:

$$wt\% = \frac{N_a \times M_{CO_2}}{M_{system}} \times 100 \quad (9)$$

where N_a represents the number of adsorbed CO₂, M_{CO_2} is the mass of CO₂ molecule, and M_{system} is total mass of the system including the SWCNT and the gas molecules. The adsorbed CO₂ molecules were estimated by summing CO₂ inside the cavity and those that were located at a distances of 7 Å from the SWCNTs surfaces [39,49,50]. SC gives us an idea regarding the amount of adsorbate that can be captured by a given amount of adsorbent at constant temperature. SC of a material is commonly expressed as a percentage by weight (wt%). At the end of each simulations, taking into account of three different chiralities and three different temperatures; the gravimetric densities and van der Waals (vdW) energy at NVE ensemble are listed in Table 2. Note that the temperatures shown in Table 2 are the average temperatures during the MD simulations, not the initial ones.

We observe that the CO₂ storage capacity is inversely proportional with the temperature, the CO₂ molecules are increasingly desorbed as the temperature increases. We can try to get an idea that at high temperature the share of vdW energy, mainly responsible for adsorption, decreases (see Table 2) as well as the the total potential energy. Since the total energy of system should be conserved at NVE ensemble, the decrease in the potential energy give rise to kinetic energy of the system. These factors leads to the weakening of the interaction between SWCNT and CO₂ molecules. As can be expected, the maximum CO₂ storage is obtained for the SWCNT (15,0) as it has the largest diameter (and therefore the highest adsorption sites) coupled with a

stronger van der Waals (vdW) attraction contribution. Therefore, with a relatively high CO₂ uptake, it is an early sign that this material is a good candidate for CO₂ capture and storage applications.

Nevertheless, simulated SC of a material is commonly reported at a constant temperature, as this condition more resemble to the real experimental conditions. Therefore, we also performed MD simulations at canonical NVT ensemble where the system temperature was constantly maintained by enforcing a thermostat through the Nosé–Hoover algorithm. The SC of the three types of SWCNTs at NVT ensemble are reported in Table 3. It can be seen that wt% trend is the same as NVE results presented in the Table 2. The gravimetric uptake is inversely proportional to temperature, whereas it is directly proportional to the SWCNT diameter and vdW attraction energy. If we compare Tables 2 and 3, however, the NVT ensemble produces lower wt% values than the NVE ensemble for all SWCNTs. This is because the temperature at NVT ensemble is kept at an initial temperature and fixed only with small deviations. On the contrary, the temperature is relaxed to provide a constant energy state for the NVE ensemble. The temperature relaxation at NVE ensemble lowers the system temperature from its initial temperature when the system is equilibrated. As the result, NVE ensemble exhibits higher wt% values and vdW attraction energy contribution than those of NVT ensemble (see Tables 2 and 3).

The total gravimetric uptake comparison between some nanoporous materials is reported in Table 4. It

shows that the (15,0) structure adsorbs CO₂ molecules up to 34.8 wt% at microcanonical NVE ensemble and 33.4 wt% at canonical NVT ensemble with an initial temperature of 273 K. This value is comparable and competitive with other materials investigated by using experimental and/or theoretical methods reported in Table 4. It can also be seen that the gravimetric values estimated from MD simulations performed using our potentials are in the same order of magnitude with the experimental results. However, all of the SWCNT gravimetric values obtained in this work are still lower than those of 3-dimensional porous carbons reported in Refs. [21] and [22], 54.3 wt% (300 K & 30 bar) and 48.1 wt% (298 K & 20 bar), respectively. This was expected to be due to the more available pores acting as adsorption sites in the 3-dimensional structure with respect to the 1-dimensional ones. The high CO₂ uptake of the (15,0) SWCNT structure can also be visually caught in Fig. 6, where the molecular configuration at the end of 10 ns simulation time is shown.

In order to justify that the inclusion of SWCNTs flexibility is important for gas adsorption, we have performed quantitative analysis of time scales for out of plane movement of SWCNT and the diffusion time of CO₂. We calculated the displacement of SWCNT diameter from its ideal value as an indication of out of plane movement of the carbon atoms of SWCNT. Figure 7 shows that SWCNT (10,0) diameter fluctuates at the time scale of ps, other SWCNTs diameters also fluctuate at the same time scale. The diffusion time of CO₂ were then calculated from the diffusion coefficients (D)

Table 2 The vdW energy (kcal mol⁻¹) and gravimetric density (wt%) of three different SWCNTs at NVE ensemble

SWCNT	d (Å)	T (K)	E_{vdW}	wt %
(5,0)	3.914	253.1	-68.63 ± 10.04	21.48 ± 3.40
		266.8	-65.00 ± 9.32	20.17 ± 3.30
		302.8	-54.03 ± 7.72	17.29 ± 2.88
(10,0)	7.828	253.2	-161.88 ± 13.05	30.60 ± 3.04
		277.8	-139.03 ± 11.66	26.04 ± 4.93
		305.8	-130.57 ± 9.86	24.43 ± 2.43
(15,0)	11.743	262.1	-232.90 ± 16.69	34.83 ± 2.66
		285.6	-208.86 ± 15.31	31.78 ± 4.57
		326.8	-180.06 ± 13.87	27.90 ± 2.29

Table 3 The amount of adsorbed molecules, vdW energy (kcal mol⁻¹) and gravimetric density (wt%) of three different SWCNTs at NVT ensemble

SWCNT	T (K)	$N_{CO_2,in}$	$N_{CO_2,out}$	E_{vdW}	wt%
(5,0)	273	0 ± 0	25 ± 4	-62.68 ± 9.81	19.66 ± 3.33
	300	0 ± 0	22 ± 4	-54.95 ± 7.53	17.65 ± 2.84
	353	0 ± 0	17 ± 4	-42.52 ± 7.19	13.70 ± 2.76
(10,0)	273	4 ± 0	38 ± 5	-146.12 ± 12.82	27.50 ± 3.04
	300	4 ± 0	33 ± 4	-129.42 ± 9.74	24.17 ± 2.58
	353	4 ± 0	27 ± 4	-110.10 ± 9.92	20.27 ± 2.58
(15,0)	273	15 ± 1	45 ± 4	-221.01 ± 16.32	33.37 ± 2.53
	300	14 ± 1	40 ± 4	-197.14 ± 13.15	30.03 ± 2.41
	353	13 ± 1	34 ± 4	-163.77 ± 11.97	25.70 ± 2.31

Table 4 Total gravimetric uptake comparison between various nanoporous materials

Materials	T (K)	P (bar)	CO ₂ uptake (wt%)	References
SWCNT (9,9)	298	30–60	21–23	[25]
MOFs	298	1	19.7	[52]
Graphene oxide (nanocomposite)	300	20	12.7	[53]
SWCNT	298	1.1	2.9	[54]
Nanoporous carbon	298	26	17.7	[55]
Nanosilicate	298	55	22	[56]
CNT (nanocomposite)	298	32.5	28.4	[57]
SWCNT (10,0)	253 <u>273</u>	21.7 <u>24.6</u>	30.6 <u>27.5</u>	This work*
SWCNT (10,0)	278 <u>300</u>	29.0 <u>32.5</u>	26.0 <u>24.2</u>	This work*
SWCNT (15,0)	262 <u>273</u>	17.1 <u>19.9</u>	34.8 <u>33.4</u>	This work*
SWCNT (15,0)	286 <u>300</u>	20.8 <u>26.5</u>	31.8 <u>30.0</u>	This work*

*Underlined data represent NVT results, while the non-underlined data represent the NVE

Fig. 6 Snapshot of final configuration for the (15,0) system at 300 K **Fig. 7** Displacement of SWCNT (10,0) diameter from its ideal value during the simulations at 273 K

reported in Table 5 by applying the Einstein's equation. We obtained that the diffusion time of CO₂ are in a range of 0.0066 to 0.0149 ps for 1 Å displacement. If we consider the diffusion of CO₂ from the edge to

Table 5 The diffusion coefficient ($10^{-7} \text{ m}^2 \text{ s}^{-1}$) of three different SWCNTs at NVE and NVT ensembles

SWCNT	T (K)	D_{NVE}	D_{NVT}
(5,0)	273	1.74	2.02
	300	1.71	2.13
	353	1.52	2.51
(10,0)	273	1.38	1.80
	300	1.76	1.60
	353	2.12	2.18
(15,0)	273	1.12	1.35
	300	1.38	1.67
	353	2.12	1.76

the center of simulation box, every CO₂ will need 0.2 to 0.4 ps (depends on the applied system) to complete the journey. It is clear that the time scales for out of plane movement of SWCNT and the diffusion time of CO₂ is still at the same order of magnitude. The surface of SWCNTs oscillates as CO₂ molecules diffuse toward it. Therefore, it has been verified that the flexibility of SWCNT indeed has a significant impact on the adsorption dynamics.

As a conclusion, having relatively high gas uptake and remarkable physicochemical properties of carbon-based materials, SWCNTs are equipped with a property that makes them potentially versatile materials competitive with other porous adsorbents to cope with CO₂ gas emission. Indeed, with an increase in diameter, other gas molecules can also be adsorbed by SWCNTs thus lowers the storage capacity of CO₂. However, if a material exhibits high CO₂ uptake, it is an early sign that this material is a good candidate for CO₂ capture and separation applications. Therefore, our future objective is to extensively investigate the application of SWCNTs in separating CO₂ molecules from CO₂/N₂ and CO₂/CH₄ gaseous mixtures saturated with H₂O component.

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