

Gas separation through Carbon Nanotubes

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Abstract Layering phenomena of carbon dioxide and methane transported through carbon nanotubes are being examined through molecular dynamics. The layering formation is investigated for carbon nanotubes ranging from (6,6) to (20,20) subjected to pressures spanning between 5-20 bar at 300 K. Well defined layers are developed both in the internal and external surface of the nanotubes for all the examined cases. It is also shown that the number of layers along with their absolute strength varies as a function of the nanotube's diameter, carbon dioxide and methane's density and gas-structure interactions. Finally, the diffusion inside the interior of the nanotubes has been examined showing a Fickian diffusion mode.

Keywords: Binary Mixtures, Adsorption, Carbon Nanotubes, Molecular Dynamics, Diffusion.

1. Introduction

Green house effect is recognized as one of the most vital environmental problems in the industrial world. Global warming is the most noticeable effect of this phenomenon with carbon dioxide possessing a vital role. Carbon dioxide is perceived to be the most blatant greenhouse gas, with a continuously increasing concentration in the atmosphere (Aaron and Tsouris, 2005). Fossil fuel power plants along with the increasing number of vehicles contribute, each one with its rate, to the 30 billion tons of CO₂ that are produced every year (Karagiannis and Soldatos, 2010). The increasingly high amounts of CO₂ emitted in the atmosphere have stimulated the interest of the scientific world towards the development of new technologies and techniques for carbon dioxide's capture and sequestration. Technological advancements, arising from these innovative strategies, have a vital role in the implementation of carbon dioxide alleviation schemes with the expectation of a wide range of socio-economic profits.

Since 1991, when Iijima (Iijima, 1991) first reported the fifth state of carbon, after diamond, graphite, amorphous carbon and fullerenes, known as Carbon Nanotubes

(CNT), numerous studies have been accomplished aiming to investigate and improve CO₂ adsorption by CNTs (Alexiadis and Kassinos, 2008; Skoulidas et al., 2002a, Skoulidas et al., 2002b; Matranga et al.). CNTs are envisaged among the the most promising nanomaterials (Baughman et al., 2003), exhibiting a wide range of exceptional properties, enclosing a wide a application envelope ranging from gas separation and materials' science (Alivisatos et al., 1998; Arora et al., 2004, Skoulidas et al., 2002b) to biology and nanoelectronics (Kim et al., 2008; Zheng et al., 2003; Star et al., 2004; Kato and Kitajima, 2010).

Over the last years, a great burst of experimental and numerical studies has been carried out for the analysis of gas filtration through CNTs (Kong et al., 2000; Bernardo et al., 2009; Tseng et al., 2009). Advanced experimental works, complimented also by computational studies, have shown that fluids can be transported inside single walled carbon nanotubes (SWNTs) orders of magnitude faster compared to classical microporous materials like zeolites (Skoulidas et al., 2002a), which are currently used for gas and liquid filtering and storage tanks. Among other characteristic properties, their very small pore size along with the almost frictionless curved

graphitic walls offer a rare combination of high transport efficiency and selectivity (Noy et al., 2007) indicating them as possible candidates for gas adsorbents (Shi2003). This inborn capability, escorts the scientific community to conduct additional studies, concerning the use of the miscellaneous carbon based materials to act as filtering membranes (Braga et al., 2007; Ten Bosch, 2005). The goal is the development of CNT membranes shaped in portable devices characterized by low weight storage with fast kinetics for fast charging and discharging the adsorbate which is stored based in the physisorption process.

Recent numerical studies, have analyzed carbon dioxide's behaviour into the interior of the CNTs (Alexiadis and Kassinos, 2008; Mantzalis et al., 2011). CO₂ molecules are mostly accumulated at the proximity of the internal walls formulating layers which follow the cylindrical geometry of the tube. The latter CO₂-phylic properties are accompanied by a hydrophobic behavior of the graphitic walls driving H₂O molecules to be more adsorbed by the external walls. CO₂-phylic properties, originate due to the fact that CO₂-CNT interactions are stronger than CO₂-CO₂. Moreover, carbon dioxide can bind in fewer adsorption sites compared to other gases such as H₂, O₂ and Ar indicating there a different adsorption mechanism (Bienfait et al., 2004) which must be further investigated.

However, in real applications carbon dioxide is found in mixtures and there needs to be separated before the sequestration process. For this reason in the present study, the adsorption process of binary mixtures containing CO₂ and CH₄ is examined. The outline of this paper is as follows. Section 2 provides a description of the MD model that has been employed. In addition, a presentation of all numerical details needed to mimic the physics of the model is given. In section 3, the layering behavior of the adsorbed molecules of the mixture in different mole fractions is presented. Section 4 presents the modes of diffusion that are developed with the flow through the nanotubes

and Section 5 provides the conclusions of the present study.

2. Model and Simulation Details

In the current work, molecular dynamics simulations have been employed for the analysis of CO₂-CH₄ adsorption by the SWNTs. The simulations have been performed using a modified version of LAMMPS package (Plimpton, 1995). Classical molecular dynamics (MD) approaches have been performed to investigate a variety of effects including the mixture's concentration and the nanotube's diameter. The innate behavior of CO₂ and CH₄ transport through SWNTs is examined, aiming to erect the limited physical knowledge concerning the layering phenomena observed close to the nanotubes' graphitic walls for the mixture. In addition, a non-systematic investigation has been held regarding the SWNT's pore size that corresponds to the optimal operational conditions of CO₂-CH₄ adsorption and under ambient values of pressure and temperature.

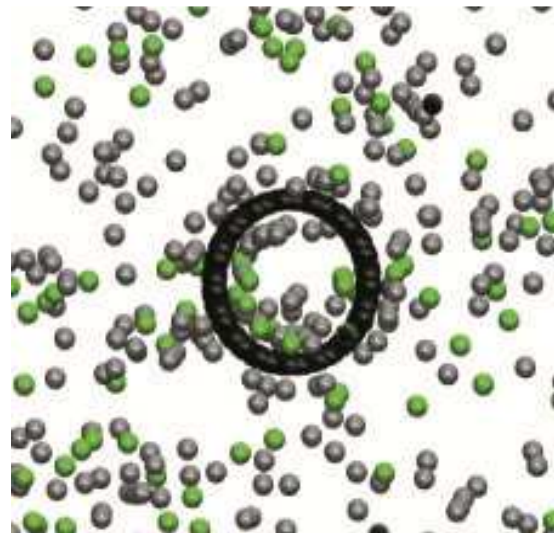


Figure 1. Snapshot of MD simulation for (16,16) at T=300 K and P=20 bar, for the equimolar mixture.

A series of armchair (n,n) SWNTs have been chosen with indices spanning from n=6,8,12,16,20 and the corresponding tube's radii, R, varying between 4.12-13.84 Å. The studied nanotubes are retained rigid, with the carbon atoms, C*, being fixed in their

equilibrium crystallographic positions. The frozen curvature of each nanotube affects numerical simulation of the flow through them infinitesimally, compared with the implementation of a flexible model which involves bond, angle, dihedral and improper terms. This assumption is in agreement with former theoretical and experimental works (Chen et al., 2008).

The computational domain has periodic boundary conditions in all three directions consisting of a cubic box with edges equal to 290 Å. The nanotubes have been placed in the center of the box, with equilibrium MD to simulate the system's evolution. The MD timesteps have been carried out, in the NVE ensemble (micro-canonical) with the temperature maintained via the Berendsen thermostat. The simulations have been performed under pressure values ranging from 5-20 bar at temperature 300 K. Before system's equilibration, the area outside the nanotube is randomly charged with argon and carbon dioxide molecules, with the mixture's total number to span from 3150 to 13300; the magnitude of the mixture's loadings along with the part numbers of the components, correspond to the studied bulk phases equilibrium partial pressures and temperatures. The choice of the initial conditions has been made so to retain in first place the mixture in gaseous state avoiding any supercritical or liquid states in the free volume, eliminating possible statistical errors. The original velocities were random numbers, chosen according to the desired simulation's temperature, based in the Gaussian distribution. All Lennard-Jones interactions were truncated at the cut-off distance $r_{\text{cut}}=9.0$ Å.

In all the tested cases, 5×10^4 time steps have been employed, with an initial time step equal to $\delta t=0.05$ fs until the system reaches equilibration after 25 ps. Additional 10×10^6 - 12×10^6 time steps have been performed, corresponding to 10-12 ns. The choice of the total simulation time depends on the size of the nanotube and the values of pressure and

temperature. For integrating the equations of motion during the MD timesteps the Verlet algorithm has been employed.

The nanotubes have been solvated with binary mixtures constituting of CO₂ and CH₄. Three mixtures have been employed in the present study. An equimolar and two non-equimolar with their mole fractions assigned to be $x_{\text{CH}_4}=0.5$, $x_{\text{CO}_2}=0.5$, $x_{\text{CH}_4}=0.75$, $x_{\text{CO}_2}=0.25$ and $x_{\text{CH}_4}=0.9$, $x_{\text{CO}_2}=0.1$. For the parametrization of carbon dioxide the spherical model proposed by Vishnyakov and Ravikovitch is used (Vishnyakov et al., 1999, Ravikovitch et al., 2000). Non-bonded interactions among CO₂ particles have been represented with the Lennard Jones (LJ) parameters being $\epsilon_{\text{CO}_2}/k_B=235.9\text{K}$ and $\sigma_{\text{CO}_2}=3.454$ Å and a mass equal to 44.010 g/mol. Previous computational studies (Alexiadis_CO2,Skoulidas et al., 2002b; Mantzalis et al., 2010) have shown that the use of a spherical model for simulating the CO₂ and its interactions with the SWNTs provides reasonable approximation compared to linear 3-site models (Murthy, Harris, Zhang, Pottoff) for pressures up to 100 bar. CH₄ has been typified as proposed by Grade et al. (Grade et al.) with the LJ potential parameters being $\sigma_{\text{CH}_4}=3.730$ Å and $\epsilon_{\text{CH}_4}/k_B=147.99\text{K}$ and mass equal to 16.042 g/mol. To represent the interactions between CNTs and the components of the mixtures, LJ potential has been used with the parameters being $\epsilon_{\text{C}^*}/k_B=28.0\text{K}$ and $\sigma_{\text{C}^*}=3.4$ Å (Alexiadis and Kassinos, 2008; Mantzalis et al., 2011). The choice of two spherical models has been made so that trends of the CNT transition radii may be easily interpreted compared with a possible use of a 3-site model for carbon dioxide. Additionally, all cross interactions have been derived based on the Lorentz-Berthelot combining rules.

3. Layering Schemes

Figure 1 shows the formation of the mixtures' components layers inside the nanotubes at temperature 300 K and pressure 20 bar inside a

(16,16) nanotube submerged into the equimolar mixture. The mixture tends to accumulate into the internal volume of the nanotube, presenting either single or double cylindrical sheets co-axial to them. Carbon dioxide and methane loadings have been covered around the axis of the adsorbate which lay at the central region of the CNTs. The internal volume of the nanotube, adapted to each case, has been virtually partitioned into a series of cylindrical shells, concentric to the carbon structure. The thickness of each axial bin equals to ($\Delta x=0.01 \text{ \AA}$), dissolving spatial deviations avoiding at the same time possible statistical errors. During the simulation, CO_2 and CH_4 molecules are continuously in motion, the averaged number densities in time, calculated in the computational layers are well defined. In distances far from the investigated CNTs, number density has not been altered by its presence, being equal with the bulk density of its case. Approaching regions close to the nanotubes, their influence becomes stronger. Possible explanation for the latter can be achieved by taking into consideration a combination of the radius of each tube along with the intermolecular and fluid-structure interactions.

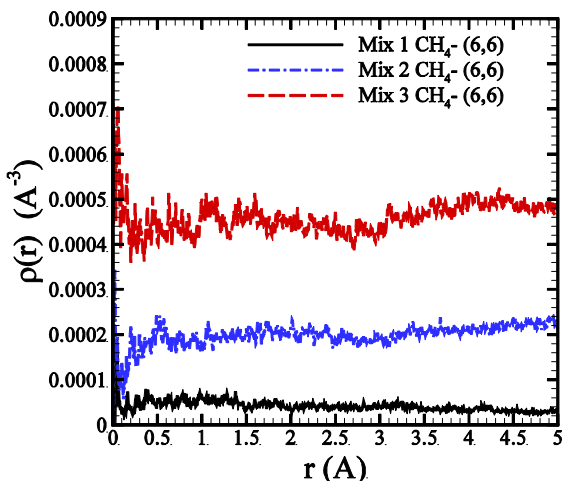


Figure 2. Internal Density profile for CNTs at $T= 300 \text{ K}$ and $P= 20 \text{ bar}$ for CH_4 into (6,6) for various mixtures.

In detail, Figures 2-7 present the layering formation, in case of four armchair SWNTs, with chirality vectors (6,6),(12,12),(16,16), at $P=20 \text{ bar}$ and $T=300 \text{ K}$ for the three studied mixtures. Figures 2-3 illustrate the density

profile that the mixture adapts inside a narrow (6,6) nanotube.

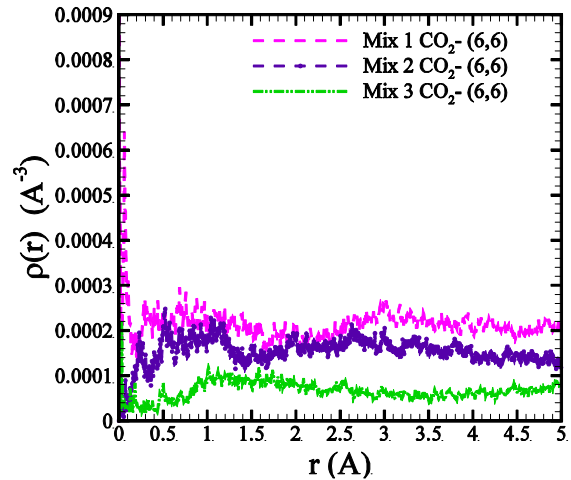


Figure 3. Internal Density profile for CNTs at $T= 300 \text{ K}$ and $P= 20 \text{ bar}$ for CO_2 into (6,6) for various mixtures.

The above produces a not clearly defined layering formation in the vicinity of the tube's axis pointing out to possible capillary condensation issues. As the diameter of the nanotube increases (cases (12,12),(16,16) different formations arising. The layering structures agglomerate near the carbon surface arranging the adsorbed molecules into cylindrical structures. In case of the (12,12) it is clear that the above trend is near its triggering radius, since the affection of each separation distance (σ_{CO_2} , σ_{CH_4}) is discrete (Figures 4-5). The differences in the above number, even if in first place are negligible, it seems that they affect the shift point of the peak values of each density layer. As x_{CH_4} increases, a secondary layer is rising with a simultaneous retreat concerning the CO_2 secondary layers. Moreover, the CO_2 preference remains stronger for mixtures with lower concentration in carbon dioxide. However, examining wider nanotubes (Figures 6-7), the strength of the influence of separate fluid-structure interactions decreases. The composition of the mixtures does not alter the layering topology, however as expected it determines the absolute values of the computed densities.

In the present work, a dual capture is observed, since both CO_2 and CH_4 are being adsorbed in

comparable portions. The latter behavior is different with the binary mixture CO₂-Ar where the adsorption capacity differs at least two scales with carbon dioxide showing a favorable trend excluding in practice Ar from the CNTs' interior (Mantzalis et al., 2011b). The aforementioned still remain in the present mixture however the differences diminish, laying at the same scale. The CO₂-phylic properties that CNTs possess dictate the adsorption without this time excluding methane. Possible reasons should be considered either the presence of H atoms or methane's weight or a combination of the above with further investigation around their physics to be required.

Figures 8-11 show the radial density profiles as function of pressure at 300 K in the internal space of the (12,12) and (20,20) nanotubes in case of the equimolar mixture. The pressure does not modify the layers' arrangements, which remain intact as previously analyzed, based in the combination of the nanotube's radius and the fluid-structure interactions. However as expected, it affects the peak values of the density layers. Specifically, as the pressure increases, the density maxima, as absolute values, are enhanced. As the pressure further increases, the density profiles tend towards a maximum value corresponding to the maximum number of molecules that can be accommodated around the graphitic walls of the nanotube. In case of CH₄ and for the (12,12) nanotube a small shift in the density maxima is noticed as pressure increases from 10 to 15 bar primarily due to the increased number of particles accommodated inside the CNTs walls (Figure 10). On the other hand concerning carbon dioxide for pressures higher than 15 bar seems to approach the maximum capacity levels and therefore the peak density value moves towards its maximum (Figure 11).

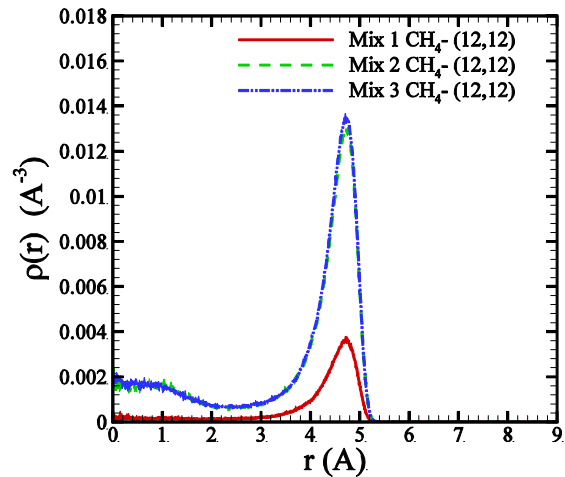


Figure 4. Internal Density profile for CNTs at T= 300 K and P= 20 bar for CH₄ into (12,12) for various mixtures.

Examining a nanotube with a wider pore (16,16), for an equimolar mixture, the CO₂-adsorption performance remains clear as in all the studied cases. Number density between Carbon dioxide present an almost double capacity compared with methane (Figures 8-9) which bulwarks the latter.

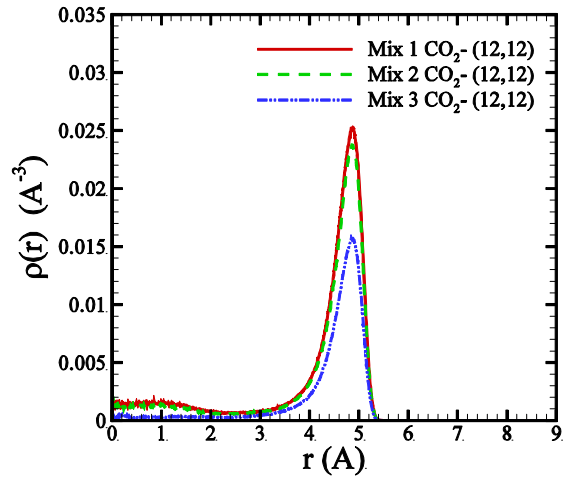


Figure 5. Internal Density profile for CNTs at T= 300 K and P= 20 bar for CO₂ into (12,12) for various mixtures.

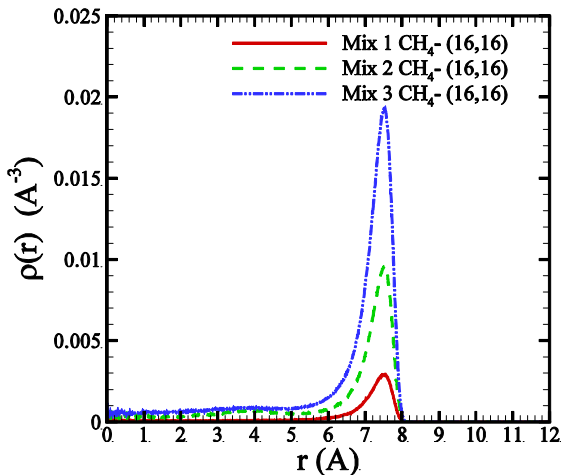


Figure 6. Internal Density profile for CNTs at T= 300 K and P= 20 bar for CH₄ into (16,16) for various mixtures.

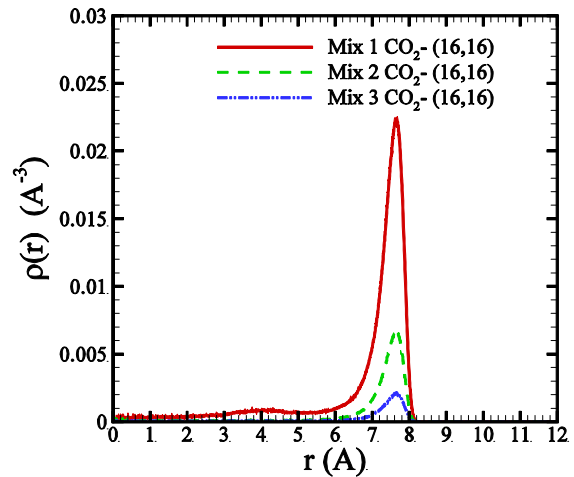


Figure 7. Internal Density profile for CNTs at T= 300 K and P= 20 bar for CO₂ into (16,16) for various mixtures.

Examining carefully the layering behavior of CH₄, a double layering scheme arises with a simultaneously increase in pressure. Pressures around 10 bar give birth to a secondary layer near the axis of the nanotube. As the pressure continues to increase, a different trend is being developed. At P=15 bar more methane particles accumulate in regions closer to the graphitic walls with the layer near the axis to weaken. Further increase at P= 20bar alters the behavior having a simultaneous increase in both layers. On the contrary, no double layering schemes have been commenced, in case of carbon dioxide. This is a major difference on the layering topology with a single fluid case where in case of a CO₂-CNT system in a (16,16) system a secondary layer appears (Mantzalis et al., 2011). It seems that it is blocked by the simultaneously insertion of the methane inside the nanotube but further investigation is needed. Examining a non-equimolar mixture the layering topology remains intact with the only differences to be the densities' magnitude of each case which is explained by the different mole fractions that studied in the second mixture.

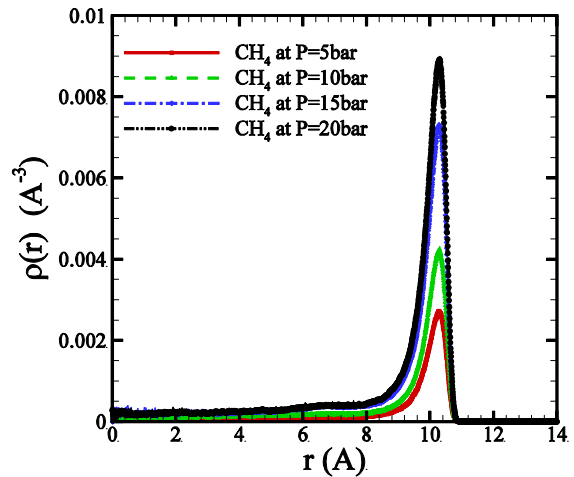


Figure 8. CH₄ Internal Density profiles for equimolar mixture at T=300K for P=5-20bar for (20,20) nanotube.

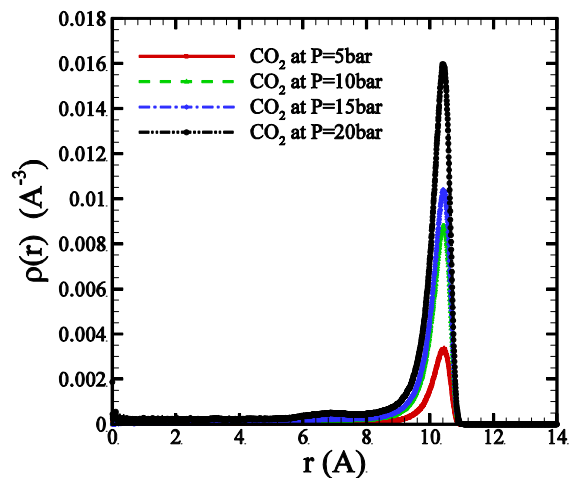


Figure 9. CO₂ Internal Density profiles for equimolar mixture at T=300K for P=5-20bar for (20,20) nanotube.

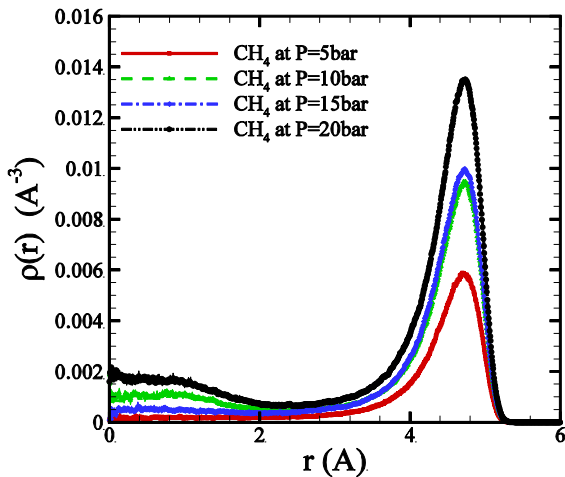


Figure 10. CH₄ Internal Density profiles for equimolar mixture at T=300K for P=5-20bar for (12,12) nanotube.

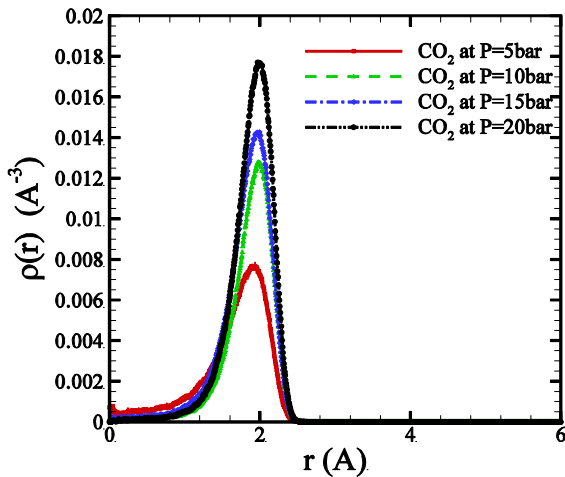


Figure 11. CO₂ Internal Density profiles for equimolar mixture at T=300K for P=5-20bar for (12,12) nanotube.

4. Diffusion

Diffusive flow monopolizes the flow physics in nanometer-scale pores, and therefore presents great interest (Mao and Sinnott, 2000). Figures 12-13 show the calculated mean square displacement (MSD) for two nanotubes at T=300 K for P=20 bar for the three mixtures. Figures 12 and 13 illustrate the same pattern for the MSDs as a function of time.

The characterization of diffusion's type is one of the most important issues for this kind of studies. If MSD presents a linear trend as a function of time then the diffusion is known as Fickian; a failure in fitting linearly MSD through time indicates the presence of

another mode of diffusion. It can be either single-file diffusion (SFD) or transition-mode diffusion (TMD) (Mao and Sinnott, 2000; Chen et al., 2010) depending on the relation that can be used for the fitting.

Figures 12 and 13 present the axial MSD changes as time increases inside (6,6) and (20,20) nanotubes. Examining the entire simulation time it is observed that the linear behavior is dominated just like in case of the (20,20) suggesting the presence of a Fickian diffusion. However, as shown in previous studies (Chen et al., 2010) in early stages of simulations of narrow pores a period of SFD and TMD is noticed before the Fickian. The latter has been also identified in the present study up to 100 ps but due to the total simulation time cannot be lucid in the Figures 12 and 13. The latter is more obvious in case of (6,6) which possess a more narrow pore. Additional studies are needed in shorter time periods for exploring in more detail the transition times for each case.

Considering the dependence of the MSD on the composition of the mixture, both in narrow and wider pores, the behavior remains intact. Neither the chirality, nor the internal radius affect the mode of the diffusion that each component exhibit. Diffusion is not affected by the composition of the studied mixtures suggesting that it depends on the pore's width along with the fluid-structure interactions and the values of pressure and temperature. However in case of a wider pore, like the (20,20), the diffusion of CO₂ is lower than methane's in case of the equimolar mixture indicating a higher degree of movement.

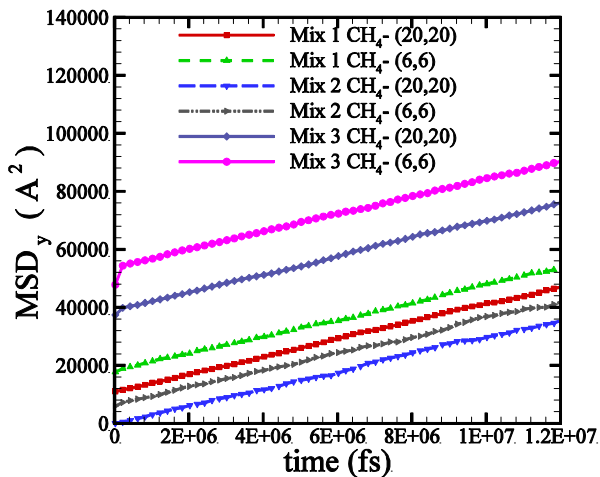


Figure 12. Axial MSD for three mixtures into two CNTs at T=300 K and P=20 bar for CH₄.

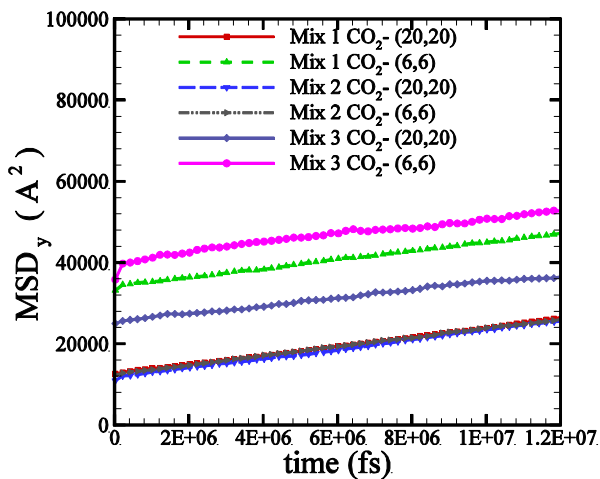


Figure 13. Axial MSD for three mixtures into two CNTs at T=300 K and P=20 bar for CO₂.

5. Conclusions

To conclude, the present work illustrates a well defined cylindrical formation for the mixtures' components, which mainly depend on the tube's size and the gas-carbon interactions. The formation of carbon dioxide and methane layers in the proximity of the cylindrical graphitic walls has been analyzed for pressures ranging from 5-20 bar at T=300K. It has been shown that the density behaviour is a function of the central radius. The latter also defines the mode of diffusion into the interior of the nanotubes.

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