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Equilibrium Molecular Dynamics Modeling of Diffussion and Adsorption of Fluids in Armchair Single Walled Carbon-nanotube

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Abstract

The aim of this paper is to study adsorption and diffusion of gases and liquids especially Argon and Carbon-dioxide in single walled carbonnanotube at room temeperature using equilibrium molecular dynamic simulation. The simulation domain is developed by the large atomic/molecular massively parallel simulator (LAMMPS). The domain consists of a simulation box of volume 100x100x100$\mathring{A}$ having periodic boundary conditions at the x, y and z direction.The adsorption and diffusion of different chirality of carbonnanotubes are reported. The Molecular Dynamics Simulation (MD) result shows that single walled carbonnanotube have affinity to attract carbon dioxide to itself than argon, with argon acting as a catalyst for adsorption of more Co_2 confirming a high adsorption at higher loading. The highest adsorption and diffussion inside the Single-walled carbon-naotube (SWCNT) was determined at certain loading and temperature. The SWCNT is assumed to be rigid due to the fact that, flexibility is insignificant and can increase computational time. This study will bring about a better understanding of storage and filtering of gases in SWCNTs and so leading its usefullness in applications such as gasification for jet engines, Co_2 removal in the international space station, desalination for water systems, air purification, longer space batteries and enhanced oil recovery.

I. INTRODUCTION

Frequently flying modules and nodes on board the international space station (ISS) to meet carbon-dioxide/oxygen eradication requirement will be too expensive making their application impractical. Currently, the (ISS) have the carbon-dioxide removal system (CDRA), multifilters for advanced water recovery and the new Sabatier assembly. These systems and process ensure the safe removal of Co2 from the ISS with the use of zeolite filters. There are recent ways gases including carbon-dioxide and argon are removed from a collection of gases they include, chemical adsorption, distillation and purification [2-6]. These methods have been reviewed, and purification using membrane and adsorption with porous materials were found favorable to selective distallation and transport phenomena. The process of the removal of Co_2 in the ISS is shown in Fig.1.

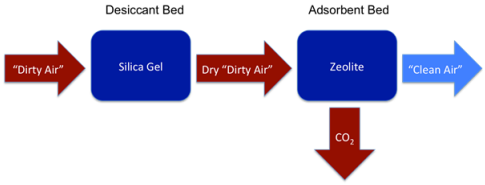


Figure 1. Co_2 Removal process in the ISS. Source: [21]

The adsorptive process favors high separation while the purification process aligns to timescale in the process of separation. These processes depend on optimization, operating conditions and performance considering range of pressures, phase constituents and temperature. Carbon-nanotube (CNT) have been studied widely as having ability to retain and attract Co_2 than zeolite because of its smaller and attractive pore [7-9]. One of the most interesting features of CNTs is the ability to engineer its pores for gas-phase separations [10]. Carbon-nanotube pores of range 0.5-2.0nm can be achieved in the process of synthesis. Pores of this size can adsorb gases such as (Co_2, N_2,CH_4, Ar and other green house gases), that means CNTs can be used to select these gases based on their adsorptive energies. Cabon-nanotubes poses a challenge in the process of separation of Co_2 and Air due to its multiscale confuguration, therefore its detailed studies will answer some questions about the phenomena that takes place in the nanoscale, and how they can be used in engineering applications. Molecular Dynamic Simulation studies on diffusion and adsorption are not very common, but have been studies by a few including [11-17] who studied molecular dynamics of diffusion in cylindrical pores with smooth walls. The Maxwell-Stefan model and molecular dynamics have been used to determine the diffusion coefficients for fluids inside zeolite pores [18]. These studies have allowed for the estimation of diffusivities of binary mixtures.

II. COMPUTATIONAL PROCESS

The molecular dynamic technique is used to simulate the sytem domain. This approach is a classical/deterministic simulation method as opposed

to the Monte-Carlo method that is classical, but stochastic. Particles in this method are modeled by newton's equation of motion;

$$f_i = \frac{\partial^2 (m_i r_i)}{\partial t^2} \tag{1}$$

Where r_i represents the position of particle i with a mass m_i and f_i which describes the force acting on the particle. The simulation domain consists of single-walled carbon-nanotube with a basic geometrical structure of hexagonal carbon. CNTs are formed from vapor of one carbon atom layer rolled into a graphene tube. A chiral vector usually describes the kind and size of the CNTs, (m,n) based on a basis angle $ma_1 + na_2$. The chiral length describes the diameter of the CNT [19]. The hamiltonian mechanics describes the dynamics in the system and is expressed as;

$$H\left(\{r_i\};\{p_i\}\right) = V\left(\{r_i(t)\}\right) + \sum_{i=1}^{3N} \frac{(P_i t)^2}{2m_i} \tag{2}$$

The trajectories and velocities of the particles are determined by a verlet algorithm. The lennard jones pair coefficient is choosen for the simulation and is given as;

$$V_{ij}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{3}$$

Where r_{ij} is the distance of two atoms, ε, lennard jones energy depth and σ is the length scale.

Table 1 shows the pair coefficients for the Lennards jones potentials.The Co_2 was parametrized with a model proposed by [20].

A simulation of CNT configuration of (10x10) and (16x16) with length of $60\overset{o}{A}$ is chosen with periodic boundary conditions. The nanotube was situated in the center of the box with equilibrium MD applied to simulate the system configuration. The non-bonded interaction of Co_2 is described by the lennard jones model with $\varepsilon_{Co_2}/k_B = 235.9K$. The microcanonical (NVE) ensemble with Berendsen thermostat is applied. The simulation was performed with pressure ranging from 5bar-40bar at temperature of 300K. A lattice spacing of $3.5\overset{o}{A}$ and cut-off $r_c = 3\overset{o}{A}$ was implemented. 50ps equilibration time and 1fs simulation time was chosen with a time step of 0.005τ. The initial conditions are chosen so that the formation of the liquid state or supercritical state in free volume will be prevented. The Maxwel Boltzman distribution is applied with random velocity to set the temperature at the desired target.

IV. RESULTS

Adsorption isotherms of 100% argon in two chiralities of 10x10 and 16x16 armchair single-walled carbon-nanotube (SWCNT) were first obtained from molecular dynamic simulation. Fig. 2 shows the density of 100% argon at single loading of 6000atoms as a function of the nanotube diameter. The adsorption layers of mixtures of pure Ar inside the CNT at temperature of 300K with pressure of 40bar is also shown. The gases are seen to have three adsorption sites inside the CNT. The maximum density peak with loading of 6000atoms is seen to form near the center of the CNT.

Site	E(kcal/mol)	σ(A
Ar-Ar	0.2379	3.405
C-Ar	0.1361	3.400
C-Co_2	0.3965	3.405
Ar-Co_2	0.2369	3.400
Co_2-Co_2	0.2359	3.500

Table 1. Pair Coefficients for LJ Interactions

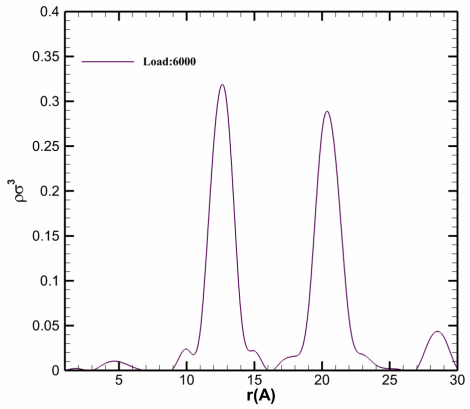


Fig 2. Adsorption of Argon in 16x16 SWCNT

Fig. 3 shows the number density of 100% Argon adsorption for 10x10 CNT with atomic loadings ranging from 250-2000. Higher loading is seen to increase the density of the gases with the highest loading obtaining a maximum peak. At the highest loading, more argon atoms are seen to accumulate near the CNT walls with weak peaks formed. The position of layering remains constant, irrespective of the amount of loading. At different loadings, the adsorption site shifted slightly with attraction between the layers of the Argon atoms.

It was observed that as the loading increases the density of the Argon atoms increased in the (10x10) armchair carbon-nanotube but the adsorption site remains the same.

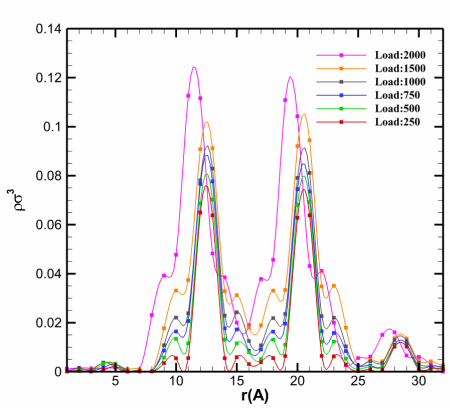


Fig 3. Adsorption of Argon of various loading in 10x10 SWCNT

Fig. 4 shows loadings of 25% argon and 75% carbon-dioxide atoms in (10x10) SWCNT. This figure shows that the adsorption site is between $8\overset{o}{A} - 16\overset{o}{A}$, with the highest density peak being the highest loading of mixture of 1500 Argon atoms and 4500 Co_2 atoms. The combination of Ar-Co_2 modifies the arrangement and position of the arrangement and position of the layerings. The adsorption site is reduced to one with density peaks seen to be stable and higher, confirming sustained Co_2 adsorption performance inside the interior of CNTs in the presence of Argon gases.

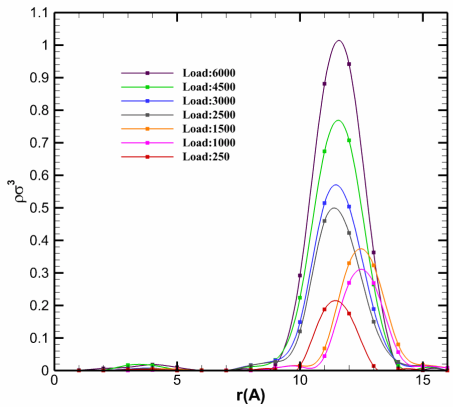


Fig 4. Adsorption of Ar-Co_2 for (10x10) SWCNT

Fig. 5 shows 50% Argon and 50% Co_2 adsorption for (16x16) SWCNT at 300K. The radial density profile with atomic loadings ranging from 250-6000 atoms of mixtures of Ar-Co_2 is presented. The CNT shows an increase in density maxima as the loading increases. However with a single and smaller density peak and number compared to all loadings of 10x10 SWCNT in Fig.3. Fig. 4 also shows that the adsorption site is between $9\overset{o}{A} - 15\overset{o}{A}$, with the highest density peak being a combined loading of 1500 Argon and 4500 Co_2 atoms, situated in the interior of the 16x16 SWCNT. This shows that Co_2 is adsorbed more than Ar, with argon atoms acting as a catalyst for more adsorption of carbon-dioxide.

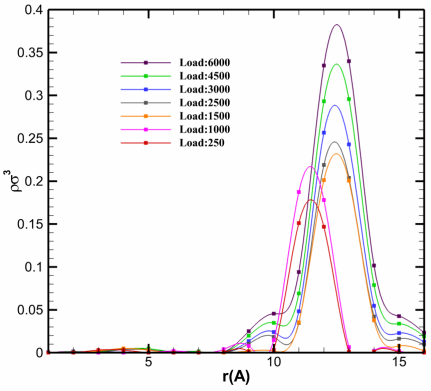
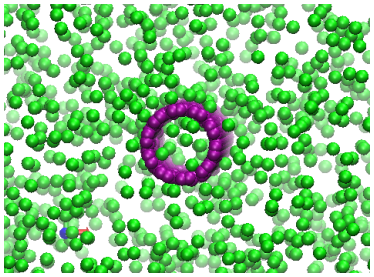


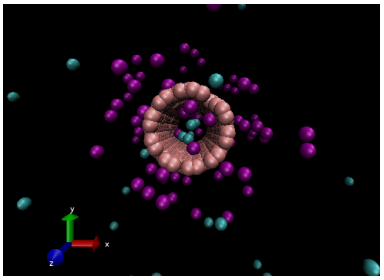
Fig 5. Adsorption of Ar-Co_2 for (16x16) SWCNT

Fig 6(a) and Fig 6(b) Shows the rendered image of 16x16 SWCNT at 300K with 100% argon atom, 25% argon and 75% Co_2. From the figure, it can be observed that more Co_2 interacted with the inside and outside walls of the carbon-nanotube because of its strength of attraction to the walls of the CNT.

It is shown that as the loading of the atoms increases according to their ratio the density peaks increases. This means that with the increase in loading of the mixtures, the concentration of Co_2 on the SWCNT wall increases in both the (10x10) and (16x16) SWCNT and the adsorption density increases. The adsorption of the Co_2 in the carbon-nanotubes decreases as the loading of argon increases for higher chirality. The argon atoms are smaller than Co_2 and less attracted to the walls of the CNT with the internal pore of (16x16), large enough to accommodate both atoms, the Co_2 is seen to always dominate in the process of adsorption.



a) Single Argon loading



b) Argon-Carbon-dioxide Loading

Fig 6. Molecular rendering of 16x16 SWCNT a) Single Argon for 6000 atoms Loading b) 75% Argon-25% Co_2 Loading for 250 atoms at 300K.

V. CONCLUSION

A good behavior of Co_2 removal using SWCNT has been reported. Carbon dioxide was found to stick to the walls of the nanotube more than argon even though argon concentration is higher than Co_2. The argon particles are seen to act as a catalyst for higher adsorption and removal of Co_2. SWCNT has been shown to have higher tendency of trapping Co_2 in the presence of Argon, in and out of its pores making it a good filter. The adsorption of these gases takes place in a particular site depending on the composition and ratio of these gases, giving the possibility of engineering and increasing these sites. Diffusion process was also observed to take place inside the pore of the SWCNT. The length of the SWCNT does not affect the adsorption instead the adsorption is influenced by the chirality, loadings of the gases and temperature which is in agreement with [2]. Therefore, carbon-nanotubes can be developed as a membrane and filter for removal of Co_2 in the international space station with a possibility of replacing existing zeolite absorbent bed and LiOH canisters.

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