Single species transport and self diffusion in wide SWCNTs

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We model and simulate gas flow through nanopores using a single-walled carbon nanotube model. Efficient protocols for the simulation of methane molecules in nanotubes are developed and validated for both the self-diffusivity, following a pulse perturbation, and for the transport diffusivity in an imposed concentration gradient. The former is found to be at least an order of magnitude lower than the latter, and to decline with increasing initial pressure, while the latter increases as the pressure gradient increases until it reaches an asymptotic value. Our previous analytic model, developed for single file diffusion in narrow pores, is extended to wider pores for the case of single species transport. The model, which predicts the observed numerical results invokes four regimes of transport. The dominant transport is by ballistic motion near the wall in not too wide nanotubes when a pressure gradient or concentration is imposed; this mode is absent in the case of self-diffusion due to periodic boundary conditions. We also present results from systematic comparisons of flexible versus rigid tubes and explicit atom versus effective atomic potentials.

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I. INTRODUCTION

Understanding molecular diffusion through porous materials is fundamental for the utilization of these materials in industrial applications involving gas separation and catalytic processes. Since the discovery of materials such as Single Walled Carbon Nanotubes (SWCNTs)\textsuperscript{3}, interest in gas transport through nanopores has increased.\textsuperscript{6–10} This diffusion is usually characterized by diffusion coefficients which describe its physical nature. The Brownian motion of molecules under macroscopic equilibrium allows the computation of the self-diffusivity, which quantifies the time dependence of the mean square displacement of a molecule. The transport diffusivity, also known as the Fickian diffusivity, defines the macroscopic flux of diffusing molecules in the presence of a concentration gradient.\textsuperscript{11,12} The latter type of diffusivity is of interest in physical processes involving molecular mass flow, such as our present focus of transport in carbon nanotubes.\textsuperscript{13} SWCNTs play an important role in the study of molecular transport due to their unique physical properties and controllable geometry (size and helicity).

Despite the wide range of applications, understanding of the mechanism for molecular transport in carbon nanotubes is still incomplete. This is because so many factors, including the nanotube structure and diameter, dimensions of the transported molecule, system temperature and interactions between transported molecules and the nanotube surface contribute to the overall transport properties. Therefore, computational methods, such as molecular dynamics (MD) or Monte Carlo (MC) simulations have been widely applied to model transport mechanisms inside SWCNTs. These automatically account for the effect of all the above-listed relevant factors.\textsuperscript{11,13–20} There has, however, been only minimal progress towards generalizing these results into a theory that can be used for design and optimization. We now present a new approach towards achieving this goal.

Among the groups who have studied diffusion of gases inside SWCNTs using computational methods are Mao and Sinnott, who reported results on the self diffusion of pure organic molecules and their mixtures through various SWCNTs based on Equilibrium Molecular Dynamics (EMD) simulations.\textsuperscript{19,21,22} Sholl and his group have obtained results for self and transport diffusivity of light gases diffusing through SWCNTs.\textsuperscript{20} Using EMD methods, they computed self and transport diffusivity simultaneously. It has been observed that the diffusion of light gases such as methane (CH\textsubscript{4}) and hydrogen in SWCNTs is orders of magnitude higher than that in other porous materials such as zeolites.\textsuperscript{11} This is because nanotubes have continuous, smooth walls of uniform composition, whereas other pores are generally composed of several elements and have pores of different sizes and diameters. Studies of interest have also been made on carbon nanopores with a rectangular geometry\textsuperscript{23–25} and on effectively “flexible” nanotubes.\textsuperscript{26}

We model the diffusive flow of CH\textsubscript{4} molecules through SWCNTs, using both EMD and Non-Equilibrium Molecular Dynamics (NEMD) techniques, including Dual Control Volume-Grand Canonical Molecular Dynamics (DCV-GCMD).\textsuperscript{27,28} The latter technique is a combination of MC and EMD simulations and applied to maintain a gradient of gas densities between the two edges of the SWCNT. It imitates a common experimental procedure used for the determination of diffusivities through porous materials by creating a non-equilibrium steady state away from equilibrium in a molecular simulation.

In a recent paper,\textsuperscript{29} we developed a model for mul-

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ticomponent ballistic transport in a narrow SWCNT that only allows for single-file diffusion, and presented DCV-GCMD simulations for single and multi-component transport. Good agreement between our model and simulations was found. We now extend our model to wider pores where molecules can pass by each other to explain and predict the following observations: (i) The apparent transport (Fick) diffusivity is larger than self- (Einstein) diffusion by more than an order of magnitude; (ii) Transport diffusivity increases with pressure gradient while self-diffusivity decreases with pressure. In addition to verifying the assumptions of the extended model, our EMD and NEMD simulations were used to explore common computational shortcuts such as simplified potentials and rigidity assumptions. We have determined the self- and transport-diffusivity, respectively, of CH4 molecules within a rigid or flexible SWCNT. For the self diffusion, we used a detailed model of the CH4 molecule, rather than the simplified Lennard Jones (LJ) approximation that is commonly implemented. Our results show that the molecules spend most of their time near the wall, very much like in chemical adsorption, and a proper model should account for ballistic motion or for diffusion within this adsorbed layer. This scenario complements the case of single-file transport for very narrow SWCNTs, in which the effective flux of diffusing molecules that was well predicted by our model that accounts for ballistic motion, hindered by counter diffusion. In the present study, the SWCNTs are wider, allowing for one molecule to pass by another. The extended model bridges the gap between our single-file model and bulk diffusion.

After introducing our general approach in the next section, we present a theoretical analysis of self and transport diffusivities in section III. This leads to analytic expressions for diffusivities as functions of pressure or concentration. In section IV, we present our results. Section IV A summaries these and estimates parameters needed for comparison with theory. In section IV B we describe our self-diffusivity results and in IV C our transport diffusivity results, and compare both with our model predictions. In section VA we compare results of flexible and rigid tubes in order to determine whether the SWCNTs nature (rigid or flexible) affect the values of transport diffusivities. In section VB we investigate whether the atomic potentials between the H and C atoms of a methane molecule must be explicitly included or whether an effective LJ interaction would suffice. Comparisons with previous simulations for limiting cases and a discussion of optimal procedures for future studies are also given. We conclude in section VI with clear guidelines for simulation procedures for different cases and with a comparison between our extended model for wider pore predictions and simulation results.

II. SIMULATION METHOD AND INTERATOMIC POTENTIALS

We consider two armchair nanotubes in our simulations: (10,10) and (12,12) having diameters of \( r_p = 13.56 \) and 16.28 Å respectively, and lengths of \( L = 50 \) Å. The forces on the atoms are calculated differently depending on the interaction range. Short-range interactions were calculated using reactive empirical bond order (REBO) potential. This is an empirical many-body classical potential that models covalent bonding within both CH4 molecules and between molecules and the carbon nanotube. It was developed by Brenner \(^{30} \) based on potentials first introduced and parametrized by Abell \(^{31} \) and Tersoff \(^{32} \) and it is empirically derived by fitting to data sets from experiments and to ab initio calculations. The binding energy in this formalism is written as a sum over all:

\[
E_b = \sum_i \sum_{i<j} \left[ V_R(r_{ij}) - B_{ij} V_A(r_{ij}) \right]
\]

where \( r_{ij} \) is the distance between species \( i \) and \( j \), \( V_R \) is a pair-additive term that models the interatomic core-core repulsive interactions, and \( V_A \) is a pair-additive term that models the attractive interactions due to the valence electrons. \( B_{ij} \) is a many-body empirical bond-order term that modulates valence electron densities and depends on atomic coordination and bond angles. \(^{19,30} \)

The long range interactions are specified by the LJ potential\(^{12} \):

\[
V_{LJ}(r_{ij}) = 4\varepsilon \sum_i \sum_{i<j} \left( \frac{\sigma}{r_{ij}} \right)^{12} \left( \frac{\sigma}{r_{ij}} \right)^6
\]

where \( \varepsilon \) and \( \sigma \) are, respectively, the energy and size (diameter) parameters of the LJ potential. The parameters of the CH4 and C species in this study were taken from Ref.\(^{33} \). The LJ potential contributes to the energy expression after the short range REBO potential goes to zero.\(^{19} \) Therefore, the combined expression used to calculate the energy of the system is:

\[
U = E_b + V_{LJ}(r_{ij})
\]

We note that LJ is used between methane and the carbon atoms of the nanotube in all cases, irrespective of whether the bonds within the methane are modeled in detail by REBO potentials or not.

The dynamical behaviour of the system is studied in the NVT (N atoms, volume V and temperature T) ensemble either with just EMD simulations or with EMD as a part of the DCV-GCMD. The atoms follow classical trajectories, whose equations of motion are solved in this study using the third-order Nordsieck predictor-corrector algorithm\(^{12} \) with a 0.5 fs time step. In all simulations,
the temperature is constrained at 300K by a Berendsen thermostat\textsuperscript{34} with a relaxation time of 0.5 ps. In some calculations the nanotube is flexible, in others rigid. Each simulation required up to 34 hours on 32 CPUs at HLRS, Stuttgart; with a combination of MPI and OpenMP techniques.

The influence of different CH\textsubscript{4} loadings on self diffusivity was investigated. At least 15 distinct independent simulations were generated for every CH\textsubscript{4} loading to compute the value of the average self diffusivity.

To find transport diffusivities, DCV-GCMD simulations were carried out in both flexible and rigid SWCNTs for varying pressure gradients of CH\textsubscript{4}. In those simulations, NEMD data were averaged over 10 or more independent simulations in each CV, using freshly generated configurations and velocities. The system typically reaches a stationary flux profile after 3-5 ns depending on the tube loading, followed by a production time of 10-12 ns. Systems with flexible nanotubes reached a stationary flux profile after 9-10 ns after which a production time of approximately 13 ns followed. On the other hand, the system with the rigid nanotube typically reached a stationary flux profile after only 4.5-5 ns which was followed by a production time of approximately 12 ns.

The trajectories of the diffusive molecules inside the SWCNTs were visualized using the Aviz program\textsuperscript{35}, initially during program development to ensure all atoms remained within the system boundaries later on for preliminary observation of the type of diffusion modes, and finally for presentation of results.

### A. Self Diffusivity Simulations

In our initial EMD simulations of diffusion with different loadings of CH\textsubscript{4} molecules inside SWCNTs, we took into account their flexible nature. The forces on the atoms were calculated according to Eq. 3. Periodic boundary conditions were applied to the nanotube along the z axis (normal to the flow) in order to confine the molecules inside the tube. EMD was applied to the nanotube’s carbon atoms (modeling a flexible tube) as well as to the carbon and hydrogen atoms of the CH\textsubscript{4} molecules.

The simulation system was typically equilibrated using the NVT Monte Carlo method\textsuperscript{36,37}, followed by production time, ranging from 100 ps to 300 ps, depending on the amount of CH\textsubscript{4} in the tubes. The simulations required up to 26 hours on 32CPUs at HLRS, Stuttgart. The resulting trajectories were then analysed to compute the self-diffusion coefficients along the axial direction of the nanotube, which we call the z direction (see the axes shown in Fig. 1). Hence these coefficients are denoted by $D_z$. Since the motion of CH\textsubscript{4} molecules is limited in both the x and y directions, we consider only the diffusion in the z direction. Thus, $D_z$ can be evaluated from the Einstein relation for molecular motion along the z direction\textsuperscript{12}:

$$\langle \Delta z^2(t) \rangle = 2D_z t$$

where $\Delta z^2(t)$ is the square of displacement in the z-direction as a function of time $t$ and $\langle \ldots \rangle$ represents the ensemble average.
the evolution of the density profile of the molecules inside the SWCNT and making sure that it has reached a linear regime, $D_t$ can be obtained. As the simulation progresses, the net number of molecules moving from CV1 to CV2, $(N_{12})$, and from CV2 to CV1, $(N_{21})$, through the $xy$ plane at the center of the nanotube, (where $z = 0.0$) is tabulated\textsuperscript{27}. As the simulation proceeds, the step function density profile slowly washes out, reaching a stationary flux profile (no change in flow rates with time) where Fick’s law is applied. Then, the molecular flux is determined by counting the net number of molecules crossing the $xy$ plane:

$$J^z = \frac{N_{12} - N_{21}}{n A_{xy} \Delta t}$$  \hspace{1cm} (6)

where $\Delta t$ is the simulation time step, $n$ is the number of time steps, $A_{xy}$ is the area of cross section of the SWCNT, defined by $\pi (r_p/2)^2$, where $r_p$ is the diameter of the tube, defined to be the center-to-center distance between carbon atoms. Finally, $D_t$, is calculated via Fick’s law for one-dimensional flow:

$$J^z = -D_t \frac{(C_2 - C_1)}{L}$$  \hspace{1cm} (7)

We note that in our analysis in section III B, we refer to transport by diffusion. We ignored the effect of convection in our interpretation of the results. This follows previous studies in the field. It does not distort the results since they are compared with model predictions and data analyses by one model (diffusion) or another (convection). In the case of molecular or Knudsen diffusion the ratio of fluxes derived by continuum models of convection is a constant that depends on pore diameter and mean free path.

### III. THEORY

#### A. Narrow Pores

Before analyzing the present case we review the theory we developed for narrow pores\textsuperscript{29}, in which only single-file diffusion is allowed. The model was successfully tested against molecular dynamics simulations. Let us fill CV1 with ”yellow” molecules and CV2 with ”blue” molecules as in Fig. 1 of Ref.\textsuperscript{29} We developed an analytic expression for the transport probability of a yellow molecule through a narrow SWCNT from CV1 to CV2 as a function of counter transport of blue molecules from CV2 to CV1 which is determined by the operating conditions. All details were explained in our previous paper.\textsuperscript{29} We defined $f_{12}$ to be the number of molecules/sec transported from CV1 to CV2 and $f_{1N}(f_{2N})$ to be the number of molecules/sec entering the SWCNT (indicated by N) from CV1/(CV2). The actual flux of “yellow” molecules is diminished due to counter transport of “blue” ones: $f_{12} = f_{1N}\Theta$, where $\Theta$ is the transport factor. Now, the transport factor of “yellow” is the probability that a diffusing molecule will not encounter a “blue” in the pore. Defining $v$ to be the molecule velocity and assuming a uniform temperature system, the flight time is $\tau = L/v$. A better approximation would account for a velocity distribution, as we did. We define $v = v^*$ to be the smallest velocity that will allow molecules to pass through the tube. Assuming one dimensional and ballistic motion of the molecules inside the tube, the transport probability is given by:

$$\frac{f_{12}}{f_{1N}} = \frac{1}{\sqrt{\pi}} \int_{E^*}^{\infty} \left[ \frac{1}{\sqrt{E}} \exp \left( -\frac{E}{E^{*}} \right) \right] dE$$  \hspace{1cm} (8)

where $E^* = m v^*^2 / (2k_B T)$ is the threshold energy. Some manipulation on this expression\textsuperscript{29} yields:

$$E^* = \frac{16}{\pi} (f_{2N} \tau)^2$$  \hspace{1cm} (9)

Good agreement between simulated molecular dynamics results and this analytic expression were demonstrated. The decrease of $f_{12}$ as a function of $f_{2N} \tau$ is almost exponential and can be approximately fitted as:

$$\frac{f_{12}}{f_{1N}} \sim e^{-(\beta f_{2N} \tau)}$$  \hspace{1cm} (10)

where $\beta$ is a dimensionless fit parameter. This approximation will be applied below.

#### B. Theory of transport in wider pores

The theory developed in the first part,\textsuperscript{29} of this research was limited to very narrow pores, where the ratio of the pore ($r_p$) to the molecular diameter ($\sigma$ as used for the LJ potential) was $2r_p/\sigma < 2$, so that only single file
transport is possible. We showed that the simulations are well described by simple ballistic motion. Here we want to extend the model to wider pores, by considering four mechanisms which contribute to the mass flux. We analyze their relative importance and derive an approximation for each case.

There is one very simple difference between wide and narrow pores. In narrow pores the potential field has a minimum at the pore center and the transport is limited to be close to that line. In wide pores there are distinct radial zones. We expect to find a potential minimum on a cylinder inside the pore, in the $z$ direction, located at approximately $r_p - \sigma/2$. A cross section of the pore is shown in Fig. 2. Looking along the pore diameter in any direction perpendicular to $z$, the potential shows two minima at distances $\sigma$ from the outer pore wall and a maxima at the center of the pore. Indeed we find a higher density of molecules at the minimum points (as will be demonstrated later in section IV B).

In a pore subject to pressures $P_{CV1}$ and $P_{CV2}$ at its ends (with the corresponding concentrations $C_1$, $C_2$), there are two radial zones. We refer to the the outer one, $(r_p - \sigma < r < r_p)$, as the adsorbed layer, and the inner one, $(r < r_p - \sigma)$, as the bulk layer, see Fig. 2. In the adsorbed layer the motion is ballistic at low densities, and follows the rules we derived for very narrow pores. At higher densities, due to the smoothness of the potential field, we expect to find a 2-D Brownian motion. In the bulk layer, diffusion is due to collisions with the potential barrier of the wall, i.e., Knudsen with effective diameter of $r_p - \sigma$, or molecular diffusion due to 3-D Brownian motion. Obviously for large pores ($r_p/\sigma >> 1$) only the latter diffusion mechanism is important. We assume that the concentrations in the two phases are in equilibrium and are related via an isotherm.

There are four possible transport regimes, two for each radial zone (surface or bulk):

(i) Surface zone: Ballistic surface flux is not linear with $\Delta P$ or $\Delta C$ and is dependent on pore length. The flux of molecules in ballistic motion, without counter diffusion, is derived from the kinetic theory: $J_{\text{ballistic}} = C \bar{v}$, where $\bar{v}$ is the molecules average velocity. Here we employ the effect of counter diffusion derived in, so that the flux of molecules in ballistic motion takes the form:

$$J_{\text{ballistic}} = \frac{1}{4} C_1 \bar{v} \frac{f_{12}}{f_{1N}} - \frac{1}{4} C_2 \bar{v} \frac{f_{21}}{f_{2N}}$$

where $f_{12}/f_{1N}(f_{21}/f_{2N})$ is a function of a single parameter that represents the probability to hit a counter molecule, $f_{2N}(f_{1N})$ (Eq. 9). The frequency is approximately the (flux)$\times$(area):

$$f_{2N} = \frac{1}{4} \bar{v} C_2 \sigma^2 N_a$$

where the area should be approximately the area of 2 molecules and $N_a$ is Avogadro’s number.

(ii) Surface zone: Brownian 2-D surface motion follows Fick’s law in surface concentration but the diffusivity is concentration dependent. This regime has not been explicitly described in the literature, but by analogy with 3-D motion we expect the diffusion coefficient to be dependent on the molecule’s velocity and mean-free-path:

$$D_{2D} \sim \frac{1}{2} \bar{v} \lambda_{2D}$$

where the 2-D mean-free-path is derived similarly to the expression for the mean-free-path in 3-D, i.e.,

$$\lambda_{2D} = \frac{1}{\sqrt{2\pi(N/S)\sigma}}$$

The surface density of molecules ($N/S$) varies with pressure (or concentration). To predict this value we will assume an equilibrium between the two phases that is described by a Langmuir isotherm:

$$q = N/S = q_m \frac{KC}{1 + KC}$$

where the maximal adsorption capacity $q_m$ is estimated from geometric consideration, while the adsorption constant, $K$, can be estimated from experimental data or from computation. Once this information is known, the local surface flux $J_{\text{surf}}$, should follow Fick’s law (Eq. 5). Using Eq. 13, one can obtain:

$$J_{\text{surf}} = -D_{\text{surf}} \frac{dq}{dy} = -\frac{\lambda_{2D}}{2} \bar{v} \frac{dq}{dC} \frac{dC}{dy}$$

where the slope of the isotherm $(dq/dC)$ can be obtained by derivation. For simplification, we use a piece-wise-linear isotherm below,

$$q = \begin{cases} q_m KC & \text{if } C < 1/K \\ q_m & \text{if } C > 1/K \end{cases}$$

Bulk zone: (iii) Knudsen or (iv) molecular diffusion in the bulk, follows Fick’s law, where the former increases with pore diameter but is concentration-independent.
Knudsen diffusion occurs when the mean free path is relatively long compared to the pore size, so the molecules collide frequently with the pore wall. Hence, Knudsen diffusion coefficient for flow in a long straight pore can be defined as:

\[ D_K = \frac{2}{3}(r_p - \sigma) \bar{v} \]  

(18)

while the molecular diffusion occurs when the mean free path is relatively short compared to the pore size, and is described by Fick’s law as follows:

\[ D_M = \frac{1}{3} \bar{v} \lambda_{3D} \]  

(19)

where,

\[ \lambda_{3D} = \frac{1}{\sqrt{2\pi (N/V) \sigma^2}} \]  

(20)

As can be seen, molecular diffusion is pore-size-independent and declines with the increase of concentration.

Changing pore diameter \((2r_p)\) or concentration (pressure) will have a complex effect: At very low concentrations the flux through the bulk is smaller than that due to ballistic motion, so that increasing \((r_p)\) will increase the effect of the former. Increasing bulk concentration (or pressure) will push the system into 2-D surface diffusion and lead to declining surface flux.

The surface cross-section of the two radial zones (as presented in Fig. 2) are:

\[ A_{\text{outer}} = \pi \left[ r_p^2 - (r_p - \sigma)^2 \right] = \pi \sigma (2r_p - \sigma), \]  

(21)

and

\[ A_{\text{inner}} = \pi r_p^2 - A_{\text{outer}} \]  

(22)

and we will define the ratio of the inner cross section, to the total, to be \(\alpha\), i.e.,

\[ A_{\text{outer}} = \alpha \pi r_p^2 \]  

(23)

The effective total flux is:

\[ J = (1 - \alpha) \left( D_K^{-1} + D_M^{-1} \right)^{-1} \frac{dC}{dy} + \alpha \left( \frac{J_{\text{ballistic}} + p}{A_{\text{outer}}} D_{2D} \frac{dq}{dy} \right) \]  

(24)

where \(p\) is the pore perimeter. For the bulk phase the overall flux is determined as two resistances in series, while for the adsorbed phase such an approach cannot be applied since the ballistic flux is expressed as an integral property that depends on concentrations at both pore ends; we approximated the latter flow as a sum of the two mechanism. Note that the ballistic motion applies as long as hinderance due to counter diffusion is small, or when the mean-free-path is larger than the tube length,

\[ \lambda_{2D} > L \]  

(25)

while the contribution of surface diffusivity will diminish with occupancy or surface concentration \((q = N/S)\), both due to diminishing diffusivity \((\text{Eq. 13})\) and due to diminishing \(dq/dC\).

The effective diffusivity is:

\[ D_{\text{eff}} = \frac{J}{\Delta C/L} \]  

(26)

Now, let us estimate the contributions of the four diffusion regimes, mentioned above, to Eq. 26, where \(i = K, m, s\):

\[ J_i \left( \frac{dC}{dy} \right) = \begin{cases} \frac{2}{3} (1 - \alpha) (r_p - \sigma), & \text{Knudsen} \\ \frac{1}{3} (1 - \alpha) \lambda_{3D}, & \text{molecular} \\ \frac{1}{2} \alpha 2 n K \lambda_{2D}, & C < K \text{ surface} \\ 0, & C > K \end{cases} \]  

(27)

The term \(\alpha (q_m K_m/\sigma) \lambda_{2D}\) can be shown to be approximately described by \(\alpha \lambda_{3D}\), but since it’s contribution is small we will not present it. These values should be compared with that due to ballistic motion, which is derived from Eqs. 10 and 11:

\[ J_{\text{ballistic}} \frac{dC}{dy} = \frac{L}{4 (C_1 - C_2)} \left( C_1 e^{-\beta f_{2NT}} - C_2 e^{-\beta f_{1NT}} \right) \rightarrow L \]  

(28)

The limit in Eq. 28 is shown for the case of large gradients \((C_1 \gg C_2)\) and small counter effect \((f_{2NT} \ll 1, f_{1NT} \ll 1)\). At small gradients, the contribution of ballistic transport is small. Thus, Eq. 26 can be rewritten as follows:

\[ \frac{dC}{dy} = \frac{J_i}{J_{\text{ballistic}}} + \frac{J_{\text{ballistic}}}{\Delta C/L} = \]  

\[ (1 - \alpha) \left[ (\frac{2}{3} (r_p - \sigma))^{-1} + (\frac{\lambda_{3D}}{3})^{-1} \right]^{-1} + \]  

\[ + \alpha \left( \frac{L}{(C_1 - C_2)} \left( C_1 e^{-\beta f_{2NT}} - C_2 e^{-\beta f_{1NT}} \right) \right) \]  

(29)

In the limiting case \((C_1 \gg C_2)\), where the right term goes to \(\alpha L\), the most important mechanism in Eq. 29 is due to ballistic motion, since \(L \gg r_p - \sigma, L \gg \lambda_{3D}\). This term may be significantly larger than molecular or Knudsen diffusion. This explains the numerical observations in the next section.

### C. Parameter estimation

The model should use the inner radius, which is the effective radius, i.e.,

\[ r_{p}^{eff} = r_p - \frac{\sigma C}{2} \]  

(30)

where \(\sigma_C = 3.4\AA\) is the diameter parameter for carbon atoms. Then, the outer cross-section (Eq. 21) takes the form:

\[ A_{\text{outer}} = \pi \sigma CH_4 (2r_{p}^{eff} - \sigma CH_4) \]  

(31)
The fraction of the inner cross section, according to Eq. 23, is:

\[
\alpha = \frac{A_{\text{outer}}}{\pi \left(r_p^f f^2\right)^2}
\]

(32)

with \( \alpha = 0.8341 \) for (12,12) and \( \alpha = 0.9382 \) for (10,10) tubes. Using this \( \alpha \) value, one can evaluate the overall diffusivity in wider pores presented in Eq. 29 where,

\[
f_{2N} = \bar{v} \frac{C_2}{4} 2\sigma_{\text{CH}_4} N a \frac{L}{\bar{v}} = \frac{PCV^2}{4RT} 2\sigma_{\text{CH}_4} N a L
\]

(33)

\[
f_{1N} = \bar{v} \frac{C_1}{4} 2\sigma_{\text{CH}_4} N a \frac{L}{\bar{v}} = \frac{PCV1}{4RT} 2\sigma_{\text{CH}_4} N a L
\]

(34)

and

\[
\lambda_{3D} = \left( \sqrt{2\pi(N/V)\sigma_{\text{CH}_4}^2}\right)^{-1} = \left( \sqrt{\frac{2\pi}{RT}}\sigma_{\text{CH}_4}^2 \right)^{-1}
\]

(35)

The \( \beta \) value was determined by fitting the simulated results, obtained using the single file model\(^{29} \) to Eq. 10. The results yielded \( \beta = 3.28 \pm 0.38 \). Since the above diffusivity relies on length of the tube, one should account for the complete value due to tube size (Eq. 29).

IV. RESULTS

A. Summary of predictions

The analysis above makes two qualitative predictions that we will show are corroborated by the simulation results in section IV C below:

- Higher transport- than self- diffusivity values: Ballistic motion contributes only to the former, while in the self-diffusivity case its contribution is for a very short time. A self diffusion simulation starts with a local pulse of high pressure of molecules, inside the tube, leading to ballistic motion. Shortly after, molecules moving right meet those going left and the ballistic contribution ceases (recall that periodic BC were imposed). Thus, while self-diffusion (s=skill) is:

\[
D_s = \bar{v} (1 - \alpha) \left[ \left( \frac{2}{3} (r_p^e f^f - \sigma) \right)^{-1} + \left( \frac{\lambda_{3D}}{3} \right)^{-1} \right]^{-1}
\]

(36)

the transport-diffusion, (t=transport) when a large density gradient is imposed (\( C_1 \gg C_2 \)) becomes:

\[
D_t = \bar{v} \alpha L
\]

(37)

Recall that the tube length is larger than the tube radius (\( L \gg r_p \)).

- Pressure dependence shows an opposite trend in these regimes: \( \lambda_{3D} \) declines with increasing pressure, so does \( D_s \) (Eq. 36), while with decreasing pressure gradient, the contribution to transport diffusivity (Eq. 29) decreases.

In the following sections, we present detailed results both for the EMD simulations with periodic boundary conditions and for the DCV-GCMD simulations with control volumes.

B. Self Diffusivities

The self-diffusion coefficient, \( D_s \) decreases with increased pressure (Fig. 3). \( D_s \) is larger in the (10,10) nanotube than in the (12,12) one for all pressures studied, these range from 5 to 50 bar.

Fig. 4 and Fig. 5 show snapshots of the distribution of REBO modeled CH\(_4\) molecules in a (12,12) SWCNT. The motion of the molecules inside the tube is visualized using the AViz software,\(^{35} \) helping us to verify that the system behaves as expected. CH\(_4\) motion follows a normal-mode diffusion, where individual molecules can pass each other within the tubes, since the diameter of the SWCNTs considered in this section is at least 3.5 times the diameter of CH\(_4\) molecule. Furthermore, it can be seen that the molecules sometimes rotate as they diffuse in the tube resulting from the repulsion interaction between hydrogen atoms of two different CH\(_4\) molecules.

Density profiles for CH\(_4\) adsorbed in the (12,12) nanotube (Fig. 6) show that at low pressures almost all molecules in the nanotube reside in a region about some 2Å in from the wall. The density further from the wall increases with increasing pressure, but at all pressures studied the density is highest at this distance from the wall. A second fluid layer develops deeper within the tube at a pressure of about 50 bar.

This follows the kinetic theory of gases that suggests a mean free path, \( \lambda_{3D} \), of 12.8 Å at 50 bar and 128 Å for
FIG. 4. Snapshot from EMD simulations of CH$_4$ molecules diffusing in a (12,12) SWCNT under a pressure of 10 bar. The carbon atoms of the nanotubes are drawn in a smaller size, so that we can observe the molecules within the tube.

FIG. 5. Projection (along the z direction) from EMD simulations of CH$_4$ molecules diffusing in a (12,12) SWCNT under a pressure of 10 bar. The carbon atoms of the nanotubes are drawn in a smaller size, so that we can observe the molecules within the tube.

FIG. 6. Density profiles for CH$_4$ adsorbed in a (12,12) nanotube as a function of the molecular pressure.

5 bar. These values should be compared with the pore diameter of $r_p=16.28$ Å, $r_p^{eff}=14.5$ Å, $r_p^{eff} - \sigma = 10.7$ Å and pore length of 50Å employed here. Thus, Knudsen diffusion applies at small pressures. The density profiles of Fig. 6 indicate that the density of gas away from the walls of the nanotube is very low until the pressure is increased to about 30 bar. Moreover, analysis of the molecular trajectories clearly shows that the CH$_4$ molecules spend almost all of their time about 2Å the nanotube wall, justifying the two radial zones structure observed in theoretical derivation. Sample trajectories for a CH$_4$ molecule in the (12,12) nanotube at 300K and several pressures are plotted in Fig. 7. It can be seen that relatively few of the trajectories cross the pore. Molecules are effectively trapped near the pore wall leading to a high density of the adsorbed gas.

C. Transport Diffusivities

Negligible differences were found between $D_t$ values in the rigid and flexible pores for most of the pressure gradient domain (Fig. 8). The difference becomes significant only for small $\Delta P$. Thus we continued with an extensive exploration for rigid tubes only. A snapshot of a visualization from our DCV-GCMD simulation of LJ modeled CH$_4$ molecules in a rigid (12,12) SWCNT of length 50Å and a $\Delta P$ gradient of 97.5 bar is shown in Fig. 9. We carried out such simulations to calculate transport diffusivities for both (10,10) and (12,12) rigid SWCNTs for $\Delta P$ gradients of CH$_4$, varying from 5.5 to 97.5 bar and compared them with model predictions, (Figs 10 and 11).

Transport diffusivity values are much larger than self diffusivity ones and monotonically increase with increasing $\Delta P$ between the CVs to reach an asymptotic value. The asymptotic values are predicted quite well by the theory (Eq. 37) as shown in Fig. 10. One must keep in mind that the theory is for an extreme limit, and the simulations are a more realistic case. The diffusivity is higher in the (10,10) tube than (12,12) one. This is mainly due to the change in the ratio, $\alpha$. The nanotubes with the smaller diameters have a higher curvature, and therefore
V. DISCUSSION OF SIMULATION RESULTS

A. Rigid vs. flexible

From a computational point of view, simulating diffusion of gases at low density is expensive because a long nanotube is needed for the gas molecules to reach a low density\(^4^4\). This poses no difficulty if the nanotube is assumed to be rigid. However, if the flexibility of a material cannot be ignored and a full atom simulation of the material is required, the calculation becomes many orders of magnitude more expensive. Our results, as shown in Fig. 8 as well as other studies\(^4^5,4^6\) showed that in the case of gas molecules diffusing through SWCNTs, a rigid lattice is a very reasonable assumption except for low \(\Delta P\).

We can distinguish two extremes. If the wall is perfectly smooth, the collisions of the gas molecules are completely elastic and the component of the velocity parallel to the wall remains constant and hence the parallel mo-

\[ \text{FIG. 8. Transport Diffusivity, } D_t, \text{ of CH}_4 \text{ as a function of } \Delta P = P_{CV1} - P_{CV2} \text{ in flexible and rigid (10,10) SWCNT at 300K. The values of the gas pressure in the CVs are: } P_{CV1} = 7.5 \text{ bar, } P_{CV2} = 9.5, 13, 17 \text{ and } 30 \text{ bar.} \]

\[ \text{FIG. 9. Snapshot from DCV-GCMD simulation describing transport diffusion of CH}_4 \text{ molecules in a (12,12) SWCNT caused by applying a chemical potential gradient over the tube. The pressure of the gas in CV2 is 105 bar and in CV1 it is 7.5 bar. The carbon atoms of the nanotubes are drawn in a smaller size, so that we can observe the molecules within the tube.} \]

more significant distortion of C-C bonds. As the nanotube diameter increases, the effect of the curvature diminishes gradually\(^4^3\) leading to faster diffusion in (10,10) compared to (12,12) SWCNTs. The expected effective diffusivities (Eq. 29) are plotted in Fig. 11 together with the simulation results. The agreement is qualitatively impressive, but the slight systematic deviations between model and simulation which are due to counter effects of self and transport diffusion which are more significant at low pressure gradients.

\[ \text{FIG. 10. Transport Diffusivity, } D_t, \text{ of CH}_4 \text{ as a function of } \Delta P = P_{CV1} - P_{CV2}, \text{ at 300K in (12,12) and (10,10) rigid SWCNTs. The pressure values are: } P_{CV1} = 7.5 \text{ bar, } P_{CV2} = 13, 17, 30, 40, 50, 70, 93 \text{ and } 105 \text{ bar. The asymptotic values, predicted by Eq. 37, for (12,12) and (10,10) nanotubes respectively, are marked by solid and dashed lines, respectively. Error bars on the simulation data points are smaller than the symbol sizes.} \]

\[ \text{FIG. 11. Comparison of the same Transport Diffusivity results for (10,10) and (12,12) SWCNTs as a function of } \Delta P \text{ as shown in Fig 10 with points calculated from Eq. 29. The calculated points are shown by solid symbols of the same shape. Error bars on the simulations are smaller than the symbol sizes.} \]
tion would be ballistic. Diffusive behavior can then only arise from collisions with other gas molecules, which is negligible at low density. If, on the other hand, we have a sufficiently corrugated wall, these corrugations introduce sufficient randomness in the collisions to observe diffusive behavior without the need for collisions with other adsorbed gas molecules. Real SWCNTs are quite smooth, however there are always thermal fluctuations of the carbon atoms that will lead to diffusive behavior.

However at the lower pressure gradient (2.0 bar), $D_t$ in the rigid tube is greater by a factor of approximately four than the one measured in the flexible tube. In flexible tubes there are thermal fluctuations that slow the confined gas molecules by collisions with the nanotube walls more rapidly than is the case for rigid ones. This diffusive behaviour dominates the ballistic motion at sufficiently low gas loadings and leads to lower diffusion coefficients. At higher loading, intermolecular collisions determine the diffusion coefficient and one would expect little influence of the rigid vs flexible nanotube type, which is indeed the case in our results as can be seen in Fig. 8.

B. Algorithms and potentials

We now summarize and compare our results with those calculated by others with the same and different algorithms and levels of details for the potentials. We recall that ours is the sole calculation to cover such an extensive range of parameters.

Our $D_s$ values in systems modeled according to the method introduced by Mao and Sinnott\textsuperscript{19,21,22} are found to be compatible with Sholl and Johnson\textsuperscript{11} in the range of 5 to 30 bar as was shown in Fig. 3. Mao and Sinnott previously computed $D_s$ using EMD for organic molecular mixtures as well as for pure CH$_4$ at high pore loadings in flexible (10,10) and (12,12) SWCNTs at 300K. Their SWCNTs and diffusive molecules were modeled with the REBO potential, but interactions between the diffusive molecules and carbon atoms of the nanotube were characterized with LJ potentials. The $D_s$ values for CH$_4$ at high pore loadings were found to be of the order of $10^{-4}$cm$^2$/sec. This is in reasonable agreement with the values calculated in our simulation at the highest loadings. Sholl and Johnson used EMD to determine $D_s$ and $D_t$ for absorbed gases, including CH$_4$ in (10,10) SWCNTs at room temperature. However, in their calculation, the flexibility of the SWCNT was not taken into consideration and the CH$_4$ molecules were treated as spheres that interact with each other and with the carbon atoms of the SWCNT via a LJ potential. Good agreement is seen between these independent simulations. We note that our computed $D_s$ values for CH$_4$ are in quantitative agreement with the results published by these two groups. The range of pressure in the Sholl and Johnson $D_s$ calculations ranges between infinitely dilute (close to 0 bar) and 30 bar for CH$_4$, whereas in our calculations the pressure spans from 5 to 50 bar. The $D_s$ values of CH$_4$ for the (10,10) SWCNT, according to Sholl and Johnson, were found to be of the order of $\sim 10^{-5}$cm$^2$/sec, in the pressure range of $\sim 5$ to 30 bar.

Sholl and Johnson used the NEMD method of Theodorou\textsuperscript{47}, called gradient relaxation MD (GRMD) simulation, to compute $D_t$ of light gases in porous material including SWCNTs at room temperature\textsuperscript{11}. The $D_t$ values of CH$_4$ in (10,10) SWCNT, according to Sholl and Johnson, were found to be of the order of cm$^2$/sec. Keil and Dürren\textsuperscript{38}, on the other hand, used DCV-GCMD simulations to determine the transport diffusivity of CH$_4$/CF$_4$ mixtures in rigid MWNTs at 300K\textsuperscript{38}. In their simulations, LJ spheres were used to model the molecules as well as the carbon atoms in the nanotube. In addition, they applied a thermal scattering algorithm, developed for transport through model carbon membranes\textsuperscript{48}, to the molecules. This algorithm assumes that molecules reach complete thermal equilibrium with the pore wall and are re-emitted in a random direction following collision with the wall\textsuperscript{20}. This technique instantly decorrelates molecular momenta upon collision with a pore wall, leading to slow diffusion. $D_t$ values measured in their simulations are of the order of $10^{-4}$cm$^2$/sec. Our simulation contains techniques from the two methods mentioned above: we model the nanotube according to Sholl and Johnson\textsuperscript{11} and simulate transport diffusion within the tube according to techniques used by Keil and Dürren\textsuperscript{38}. Our simulations predict that $D_t$ for CH$_4$ in (10,10) and (12,12) SWCNTs are of magnitude of $\sim 10^{-2}$cm$^2$/sec, an intermediate result between the results published by Keil and Dürren\textsuperscript{38} and Sholl and Johnson. In addition, one should keep in mind that we used a different value of L from those two methods, and as was demonstrated in Eq. 29, L affects the apparent diffusivity.

The flux rate of molecules diffusing through the tube increases with increasing driving force leading to enhanced ballistic motion dominating the diffusive behavior caused mainly by intermolecular collisions since the tube is rigid. As a result $D_t$ increases until the pressure difference applied between the CVs creates a driving force that causes the nanotube to reach saturation at steady state. On the other hand, $D_s$ is evaluated when the CH$_4$ loading within the flexible tube has reached an equilibrium. As the loading of molecules within the tube increases, the number of collisions with other molecules and with the walls increase leading to enhanced diffusive behavior resulting in lower $D_s$ values, see Eq. 25.

VI. CONCLUSIONS AND SUMMARY

We have implemented classical EMD and NEMD techniques to investigate self and transport diffusion of CH$_4$ molecules at room temperature inside SWCNTs at various tube loadings. Results show that the former is at least an order of magnitude lower than the latter and it declines with initial pressure, while the latter increases with pressure gradient reaching an asymptotic value. We
introduce a model for transport of single species in both narrow and wide pores which extends our previous model that was limited to single-file diffusion. The model accounts for four regimes of transport and explains the qualitative features listed above; it also predicts well the observed values. In not too wide SWCNT the dominant transport is by ballistic motion near the wall when a pressure gradient or concentration is imposed, while it is absent in the case of self-diffusion.

A comparison of our results with other studies, shows that: taking into account the intermolecular bonding of CH₄ (i.e., using a REBO modeled molecule) has no meaningful effect on the mean-squared displacement of a molecule after time t compared with the LJ modeled molecule. Modeling CH₄ molecules as uniform spheres with the LJ parameters is indeed a good approximation when calculating their self diffusivity in a SWCNT.

Our DCV-GCMD simulations of LJ modeled CH₄ inside a fully flexible SWCNTs demonstrate that nanotube flexibility has a significant influence on transport-diffusivity at low pressure gradient ∆P < 2 bar. At higher ∆P, the diffusive behaviour is mainly determined by the intermolecular collisions and the type of the tube has only a small influence on the transport diffusion coefficient.

Modeling the observed behavior is quite complex. We account for diffusion in the fluid phase and for surface diffusion. We ignored transitions between the two phases, bearing in mind that even the phases concept may not be a rigid distinction for such narrow pores. The simulations show that most molecules stay within the adsorbed layer, and under such conditions the problem may be reduced to a 2-D problem. The probability of escaping the adsorbed phase requires knowledge of the potential barrier. Due to the potential smoothness of SWCNT, the velocities of adsorbed molecules, v, are high, and similar to their values in unconfined spaces (630m/sec for methane at 300K).

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