

Transport Diffusion of Gases Is Rapid in Flexible Carbon Nanotubes

Haibin Chen,[†] J. Karl Johnson,^{‡,§} and David S. Sholl^{*,†,§,||}

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213,
Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261,
National Energy Technology Laboratory, Pittsburgh, Pennsylvania 15236, and Division of Chemical
Engineering, University of Queensland, St. Lucia, QLD, 4072, Australia

Received: November 28, 2005; In Final Form: December 25, 2005

Molecular dynamics simulations of rigid, defect-free single-walled carbon nanotubes have previously suggested that the transport diffusivity of gases adsorbed in these materials can be orders of magnitude higher than any other nanoporous material (A. I. Skoulidas et al., *Phys. Rev. Lett.* **2002**, 89, 185901). These simulations must overestimate the molecular diffusion coefficients because they neglect energy exchange between the diffusing molecules and the nanotube. Recently, Jakobtorweihen et al. have reported careful simulations of molecular self-diffusion that allow nanotube flexibility (*Phys. Rev. Lett.* **2005**, 95, 044501). We have used the efficient thermostat developed by Jakobtorweihen et al. to examine the influence of nanotube flexibility on the transport diffusion of CH₄ in (20,0) and (15,0) nanotubes. The inclusion of nanotube flexibility reduces the transport diffusion relative to the rigid nanotube by roughly an order of magnitude close to zero pressure, but at pressures above about 1 bar the transport diffusivities for flexible and rigid nanotubes are very similar, differing by less than a factor or two on average. Hence, the transport diffusivities are still extremely large compared to other known materials when flexibility is taken into account.

I. Introduction

The diffusion rates of molecules adsorbed in nanoporous materials are central to the utility of these materials in a number of industrial applications for gas separations, including pressure- or temperature-swing adsorption and membrane-based separations.^{1–5} Materials that allow extremely rapid gas diffusion while also exhibiting appreciable adsorption selectivities would be of great interest for overcoming the limitations of well-developed materials such as polymeric membranes.⁶ Based on this observation, the prediction from molecular dynamics simulations that gas diffusion in single-walled carbon nanotubes (SWNTs) is extremely fast has drawn considerable attention.^{7–19} This prediction was first made by us based on molecular dynamics simulations of gas diffusion inside *rigid* nanotubes.⁷ These simulations must overestimate the diffusion coefficients of adsorbed molecules, since they neglect scattering of molecular momentum due to energy transfer with the nanotube during collisions with the nanotube.

Before going further, it is useful to be more precise about what kind of diffusion is being discussed. It is well known that diffusion in porous materials can be characterized by several distinct diffusion coefficients that describe different physical concepts.^{1,3,20,21} The diffusion of individual molecules is described by the self-diffusivity, D_s , which quantifies the time dependence of the mean square displacement of a molecule.

The macroscopic diffusion of mass that arises in the presence of a concentration gradient is governed by the transport diffusivity, D_t . It is the transport diffusivity that is of greatest interest in physical applications involving net mass transfer, such as membranes. The transport diffusivity is also known as the Fickian diffusivity. The self-diffusivity and transport diffusivity are both in general functions of concentration and are only equal in the limit of dilute adsorbed concentrations. In molecular models of gas diffusion in rigid nanotubes, the difference between these two diffusion coefficients at nondilute concentrations can be more than two orders of magnitude.^{7–9}

It is also useful to be precise about what we mean by diffusion being rapid. This can be accomplished by comparing room-temperature diffusion coefficients for small molecules in several classes of materials. We describe this issue in the limit of the concentration of the diffusing species being dilute, as in this limit no confusion about which diffusion coefficient is relevant can arise. In liquids, typical diffusion coefficients are 10^{-5} cm² s⁻¹ (“Toor’s law”²²). In gases, not surprisingly, much larger diffusion coefficients in the range of 0.1–1 cm² s⁻¹ are typical.²³ Typical molecular diffusion coefficients in glassy polymers are 10^{-10} – 10^{-9} cm² s⁻¹,²⁴ while diffusion coefficients varying from 10^{-11} to 10^{-4} cm² s⁻¹ have been reported for zeolites.^{1,3,25,26} Recent molecular simulations of diffusion inside metal-organic framework materials indicate that diffusion coefficients in these materials are similar in magnitude to those observed in zeolites.^{27,28} This compilation of diffusion coefficients suggests that any diffusion coefficient that is orders of magnitude faster than typical liquid diffusivities might reasonably be considered as “rapid” diffusion. Molecular simulations of small molecules

* Corresponding author. Email: sholl@andrew.cmu.edu

[†] Carnegie Mellon University.

[‡] University of Pittsburgh.

[§] National Energy Technology Laboratory.

^{||} University of Queensland.

such as CH₄, H₂, Ar, Ne, CO₂, and N₂ in rigid, defect-free SWNTs yield dilute-concentration diffusion coefficients of 0.1–1 cm² s⁻¹.^{7–12} These values are extremely large relative to other known porous materials. The origin of these large diffusion coefficients has been carefully discussed elsewhere;^{7–12,16,17} briefly, it arises because the potential energy surface defined by the interior surface of the rigid nanotubes is extremely smooth and leads to near-specular scattering of molecules colliding with the nanotube's wall. The motion of water molecules inside SWNTs has also received a good deal of attention.^{29–31} The physical mechanisms that determine the behavior of water in this nanometer-scale hydrophobic environment are distinct from those of light gases because of the strong hydrogen bonding available between water molecules.

The discussion above included only the diffusion coefficients of adsorbed molecules in the limit of dilute concentration. A more careful discussion of the rapidity of molecular diffusion in SWNTs needs to distinguish between the concentration dependence of the self and transport diffusivities at nondilute concentrations. Molecular simulations for rigid, defect-free SWNTs have shown that these two diffusion coefficients behave very differently.^{7–9} As the adsorbate concentration is increased, the self-diffusion coefficient drops very rapidly from its dilute concentration limit. To give a specific example, the self-diffusion coefficient for CH₄ in a rigid (10,10) SWNT drops from ~1 cm² s⁻¹ in the limit of dilute concentration to ~10⁻³ cm² s⁻¹ at moderate pore loadings.⁷ This strong concentration dependence arises because the low-density result is dominated by adsorbate–wall collisions while at higher densities the self-diffusivities are dominated by adsorbate–adsorbate collisions. As pointed out in ref 7, this finite loading self-diffusivity is roughly one order of magnitude larger than the largest self-diffusivities that are known in zeolites; an interesting but perhaps not earth-shattering result. Krishna and van Baten have recently shown that molecular self-diffusivities in rigid carbon nanotubes are comparable to those in bulk fluids with comparable density.³² The more interesting conclusion from ref 7 was that the transport diffusivity of CH₄ in a rigid (10,10) SWNT is ~1 cm² s⁻¹ at *all* pore loadings. These transport diffusivities are more than three orders of magnitude faster than the fastest known transport diffusivities in zeolites, even accounting for the well-known observation that transport diffusivities of adsorbates in zeolites typically increase with adsorbate concentration.^{1,3,25,26} This discussion is intended to point to the conclusion that simulations of molecular diffusion in rigid nanotubes have suggested that transport diffusion in these materials is extraordinarily rapid, while self-diffusion in the same material is larger than in other porous materials but not dramatically so.

Having discussed our previous simulation results for rigid nanotubes, we now turn to the role of nanotube flexibility in determining the diffusion coefficients of adsorbed molecules. An initial piece of information on this topic came from comparing self-diffusion coefficients for CH₄ computed in rigid SWNTs at high pore loadings in our previous work with simulations of fully flexible SWNTs by Mao and Sinnott at similar loadings.^{33,34} Although differences in simulation methodology did not allow a precise comparison, the self-diffusion coefficients computed by the two methods were similar, suggesting that in this limit neglecting nanotube flexibility was a reasonable approximation when calculating self-diffusivities. At around the same time, Sokhan, Nicholson, and Quirke compared the scattering properties of molecular trajectories inside rigid and flexible nanotubes in terms of a hydrodynamic slip length.¹⁶ Large values of the hydrodynamic slip length

correspond to individual adsorbate–wall collisions being near-specular. Although the computed slip lengths in rigid and flexible nanotubes differed by ~20%, they were both large, qualitatively supporting the idea that molecular diffusion in the low-density limit would be rapid inside flexible models of SWNTs.

Recently, Jakobtorweihen et al. revisited the role of nanotube flexibility in determining the self-diffusion coefficients of adsorbed molecules.³⁵ In the limit of low density, CH₄ self-diffusion coefficients in a (20,0) SWNT at room temperature were calculated to be ~0.2 cm² s⁻¹ in a fully flexible nanotube, compared to ~1.2 cm² s⁻¹ in a rigid nanotube. That is, at the lowest densities examined by Jakobtorweihen et al., including nanotube flexibility reduced the self-diffusion coefficient of CH₄ by approximately a factor of 6. At nondilute pore loadings, the difference between the rigid and flexible nanotubes was much less; for loadings corresponding to pressures greater than 0.1 bar CH₄, there was little difference between the two calculations. This observation is consistent with the comment above that self-diffusion in SWNTs at nondilute pore loadings is dominated by adsorbate–adsorbate collisions. A particularly useful feature of Jakobtorweihen et al.'s work was their development of a simple Lowe–Andersen thermostat that accurately represents the nature of momentum transfer between adsorbates and the nanotube wall that occurs in a simulation of a fully flexible nanotube but can be used in the enormously more computationally efficient rigid nanotube simulations. Jakobtorweihen et al. have reported results based on this concept for several spherical adsorbates in SWNTs.³⁶

The previous studies discussed above do not provide direct information on the role of nanotube flexibility on the far more interesting transport diffusion coefficient of adsorbed molecules. We reiterate that while self-diffusion in SWNTs at practical pore loadings is predicted by simulations to be moderately faster than comparable quantities in zeolites and other porous materials, transport diffusivities are predicted to be dramatically different in rigid SWNTs than in these other materials. Jakobtorweihen et al.'s results do not provide any information on transport diffusivities at nondilute pore loadings. Our aim in this paper is to use the thermostat developed by Jakobtorweihen et al. to assess the impact of nanotube flexibility on the transport diffusion of CH₄ over a wide range of pore loadings. Our main result can be stated simply: nanotube flexibility does reduce the transport diffusion coefficient relative to simulations of rigid defect-free nanotubes, but at pressures greater than 1 bar, CH₄ transport diffusivities in flexible nanotubes are only about 30% smaller than in rigid nanotubes and are still extremely fast relative to transport in other known porous materials.

II. Computational Methods

We used equilibrium molecular dynamics (EMD) to compute self- and corrected diffusion coefficients for CH₄ inside defect-free (20,0) and (15,0) SWNTs at room temperature. The details of using EMD to reliably compute these two diffusion coefficients has been described in detail elsewhere.^{7,8,37,38} Our calculations consider an isolated SWNT with periodic boundary conditions along the axial direction. Interactions among CH₄ molecules and between adsorbed molecules and C atoms in the SWNT were both represented by Lennard-Jones interactions with the same potential parameters used in our earlier work.⁷ In simulations of a rigid nanotube, a Nosé–Hoover thermostat was applied, as in our previous work.⁷ In simulations including the effects of nanotube flexibility, the nanotube was held rigid but the Lowe–Andersen thermostat developed by Jakobtor-

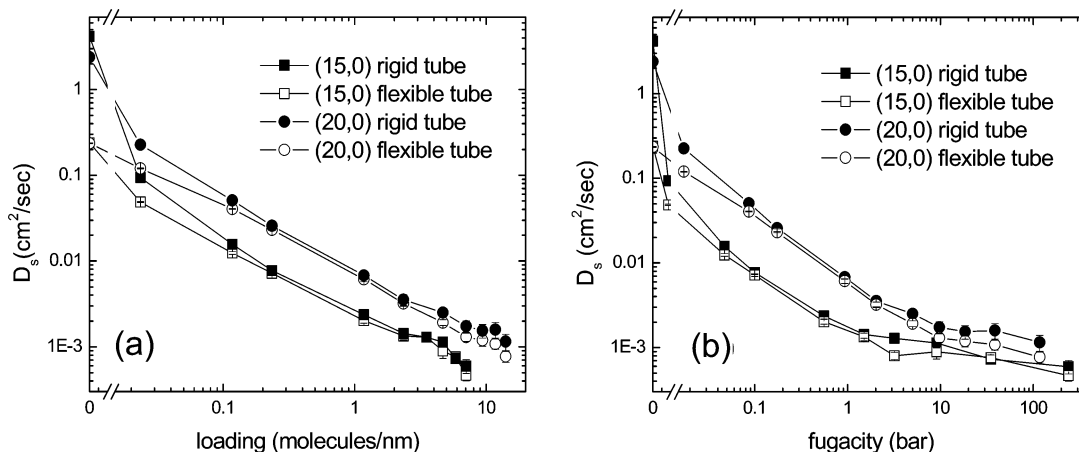


Figure 1. Loading dependence of CH₄ self-diffusion in (20,0) and (15,0) nanotubes plotted as a function of (a) adsorbate density in the nanotube and (b) bulk phase fugacity. In each case, open (closed) symbols are the results of EMD simulations with a rigid (flexible) nanotube.

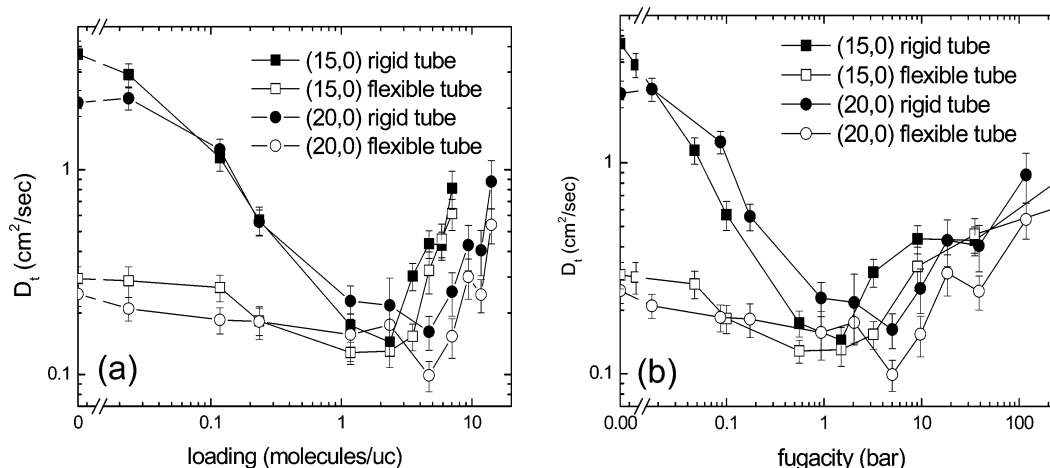


Figure 2. Loading dependence of CH₄ transport diffusion in (20,0) and (15,0) nanotubes plotted as a function of (a) adsorbate density in the nanotube and (b) bulk phase fugacity. In each case, open (closed) symbols are the results of EMD simulations with a rigid (flexible) nanotube.

weihen et al. was applied.³⁵ We refer to these simulations below simply as simulations of a flexible nanotube. This thermostat allows for momentum transfer between the adsorbed molecules and the confining nanotube and was carefully calibrated by comparisons with extensive simulations of fully flexible nanotubes at dilute adsorbate loadings.³⁵ Jakobtorweihen explored several sets of parameters for defining the Lowe–Andersen thermostat; we used the thermostat with $r_{LA} = 0.36[0.37]$ nm, $\Gamma_{xy} = 3.5 \times 10^{11} \text{ s}^{-1} [3.8 \times 10^{11} \text{ s}^{-1}]$, and $\Gamma_z = 4.7 \times 10^{10} \text{ s}^{-1} [4.0 \times 10^{10} \text{ s}^{-1}]$ for the (20,0) [(15,0)] SWNT.

Once the corrected diffusion coefficient at a specified adsorbate concentration, $D_0(c)$, is obtained from EMD, the transport diffusion coefficient at the same concentration, $D_t(c)$, is defined without approximation by^{1,3,20,21}

$$D_t(c) = D_0(c) \frac{\partial \ln f}{\partial \ln c}.$$

Here, f is the fugacity of the bulk gas phase that corresponds to the adsorbed concentration c when then bulk and adsorbate phases are in equilibrium. This derivative term, the so-called thermodynamic correction factor, can be calculated once the adsorption isotherm of the material of interest is known. We evaluated the adsorption isotherm of CH₄ in both SWNTs using transition matrix Monte Carlo (TMMC), a variant of the well-known grand canonical Monte Carlo (GCMC) method that yields the adsorption isotherm and thermodynamic correction factor for arbitrary bulk phase fugacities in an efficient manner.³⁹

III. Results

Figure 1 compares the self-diffusion coefficient of CH₄ in a rigid and flexible (20,0) SWNT. These data was reported previously by Jakobtorweihen et al.,³⁵ and our calculated results are in excellent agreement with their work. The only new feature of our data relative to Jakobtorweihen et al. is that we include the self-diffusion coefficient in the limit of $c \rightarrow 0$. Results in this limit were computed by performing simulations in which adsorbate–adsorbate interactions were neglected. In the rigid nanotube, the zero loading self-diffusion coefficient is $2.13 \text{ cm}^2 \text{ s}^{-1}$, while in the flexible nanotube, the result is $0.24 \text{ cm}^2 \text{ s}^{-1}$. The main features of Figure 1 were discussed in the Introduction. At pore loadings corresponding to bulk phase pressures larger than ~ 0.1 bar, the self-diffusion coefficients in the rigid and flexible nanotubes are essentially identical. We also present in Figure 1 calculations for the self-diffusion coefficients in rigid and flexible (15,0) SWNTs. The diffusion coefficients in the (15,0) SWNT are somewhat faster than in the (20,0) SWNT, consistent with our previous observations that diffusion in narrower SWNTs is faster than in larger SWNTs.^{7,8} The general trends for the (20,0) and (15,0) nanotubes are the same.

We report the transport diffusion coefficients of CH₄ in rigid and flexible (20,0) and (15,0) SWNTs in Figure 2. Note that the vertical axis of this figure covers a considerably smaller range than in Figure 1. In the zero loading limit, the transport diffusion coefficient in each simulation coincides with the self-diffusion coefficient. At nonzero loadings, the transport diffusion

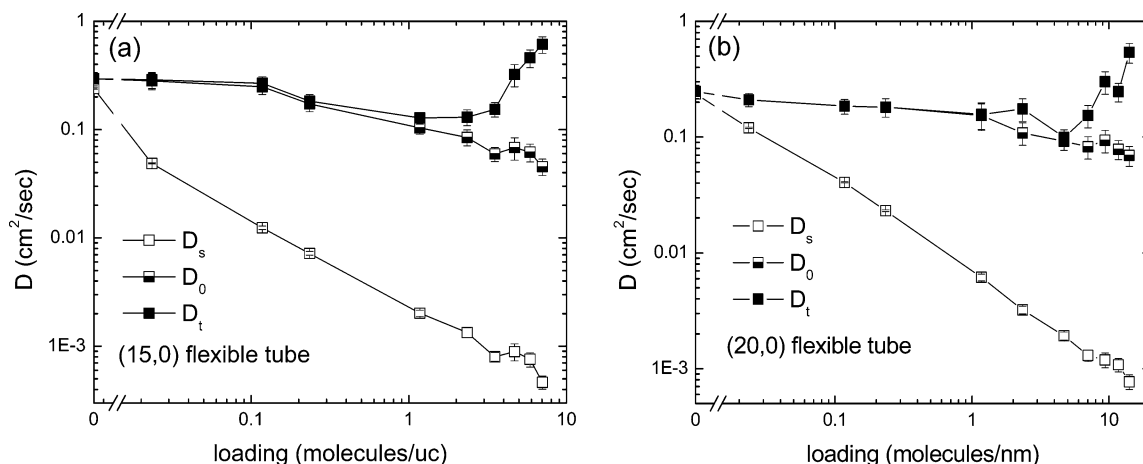


Figure 3. Loading dependence of CH_4 self, corrected, and transport diffusion (open squares, open triangles, and filled squares, respectively) in (a) a flexible (15,0) and (b) a flexible (20,0) nanotube as a function of adsorbate density.

coefficients are much larger than the corresponding self-diffusion coefficients. At low pore loadings, the rigid nanotube simulations overestimate the transport diffusion coefficient from the more realistic flexible nanotube simulations. For pore loadings corresponding to pressures higher than ~ 1 bar; however, the difference between the transport diffusion coefficients in the rigid and flexible nanotube generally less than a factor of 2. With the exception of one data point in the flexible nanotube simulations, all of the transport diffusion coefficients shown in Figure 2 are larger than $0.1 \text{ cm}^2 \text{ s}^{-1}$. Using the criterion defined above, it is reasonable to describe this phenomenon as rapid diffusion.

The computed self, corrected, and transport diffusivity for CH_4 in flexible (20,0) and (15,0) SWNTs are shown together in Figure 3. This presentation of the results highlights the very large differences that exist between the self-diffusion coefficient and the transport diffusion coefficient for moderate and high adsorbate loadings.

IV. Discussion

The main result of this paper is that the transport diffusion coefficient of CH_4 in defect-free single-walled carbon nanotubes is rapid compared to gas diffusion in other known porous materials when the flexibility of the nanotube walls is included in MD simulations. Although we have only presented results for (20,0) and (15,0) nanotubes, previous studies of gas diffusion in nanotubes of varying diameters have shown that the basic mechanism underlying the appearance of rapid diffusion in these materials is not dependent on their diameter.^{7,11} We conclude by discussing two issues, namely some complications that exist with developing detailed descriptions of nanotube flexibility and the possibility of rigorously comparing predictions from our calculations with experiments.

Although our calculations and those of Jakobtorweihen et al.³⁵ suggest that under many circumstances the influence of nanotube flexibility on the diffusion coefficients of adsorbed molecules is relatively small, it is of course worthwhile to include these effects whenever it is practical to do so. The Lowe–Andersen thermostat introduced by Jakobtorweihen et al. is an elegant way to achieve this goal. This thermostat is parameterized by performing a short time-scale MD simulation of isolated adsorbates in a fully flexible nanotube.³⁵ One minor detail that cannot be described within this approach is the possibility that the characteristics of energy transfer to and from the nanotube wall vary weakly as the adsorbate density varies. Calculations that interpreted the diffusion coefficients obtained from simula-

tions of rigid nanotubes in terms of a Maxwell coefficient for collisions with the nanotube wall have suggested a weak dependence of this coefficient on adsorbate density.¹⁰ A more significant complication associated with simulating flexible nanotubes is that recent calculations of the thermal conductance of SWNTs have raised serious doubts about the ability of classical MD to correctly describe this phenomenon.⁴⁰ Since understanding the influence of nanotube flexibility on adsorbate diffusion also involves questions of energy transfer through phonons in nanotubes, the implications of these results deserve further attention in the future.

Can the predictions of our calculations be compared with experiments? Although transport diffusion coefficients can be measured using neutron scattering methods,^{26,41–43} we know of no experiments of this type that have been performed using SWNTs. Three recent papers present measurements of permeance through membranes made up of aligned multiwalled carbon nanotubes (MWNTs).^{15,31,44} In the first paper Hinds et al. measured N_2 permeance at room temperature and low pressure.¹⁵ It is reasonable to think of these experiments as measuring N_2 permeance through the nanotubes that form the core of these multiwalled nanotubes. We have recently compared predictions made from simulations of N_2 diffusion in rigid SWNTs.¹¹ The prediction from these simulations overestimates the experimental permeance by approximately a factor of 30. However, in a more recent paper, Majumder et al.³¹ estimated that the available pore density in these membranes is actually much smaller than previously estimated by SEM measurements because many of the pores are blocked by Fe catalyst particles. Taking the revised value of the pore density, the agreement between simulations and experiments are within a factor of 2. The good agreement between simulations performed with rigid nanotubes and experimental data are an indirect indication that flexibility of the nanotubes does not dominate transport diffusion.

Majumder et al. have measured pressure-driven flow of liquids through MWNT membranes.³¹ They have compared observed flow velocities for water, ethanol, 2-propanol, hexane, and decane to expected flow velocities computed from conventional nonslip (Hagen–Poiseuille) flow. The measured flow is four to five orders of magnitude faster than that predicted by Hagen–Poiseuille flow; the apparent slip lengths for these experimental data range from 3 to $70 \mu\text{m}$ in length, many times the average nanotube diameter of 7 nm. These results are consistent with a nearly frictionless fluid–nanotube interface³¹ and reinforces our simulations indicating that transport diffu-

sivities are orders of magnitude faster in nanotubes, flexible or rigid, than in other known nanoporous materials.

This comparison with experimental data should, however, be treated cautiously, as there are several important differences between the theoretical and real situations. First, the theoretical prediction assumes that there is no influence of pore entrance/exit effects on gas permeation through the membrane. These effects are known to be negligibly small for light gases passing through some zeolite membranes, but they must necessarily increase in significance as the diffusion coefficient of the permeating species in the membrane material is increased.⁴⁵ Hints that pore entrance/exit effects might be significant for SWNTs are evident from the MD simulations of fluids entering SWNTs by Supple and Quirke.¹⁸ Unfortunately, no detailed estimates of the size of these pore entrance/exit effects for transmembrane flow through a SWNT membrane are currently available.

A second important difference between the theoretical and experimental results is that our simulations are for defect-free nanotubes, a condition that is difficult to assess and presumably difficult to achieve experimentally. TEM images of a carbon nanotube membrane embedded in a silicon nitride matrix by Holt et al. indicate a "bamboo" morphology that deviates strongly from that of a defect-free SWNT.⁴⁶ Similar characterization of the membranes used by Hinds et al. in their experiments is not available.¹⁵ Roth and Mesentseva have performed MD simulations of gas diffusion through very short SWNTs that included bends or knees.⁴⁷ Unfortunately, these simulations were at very high average temperatures and showed considerable thermal gradients over short length scales, so rigorously discussing the outcome from these calculations in terms of diffusive flux is difficult.

Although the influence of pore entrance/exits effects and morphological defects in a real membrane cannot be predicted quantitatively, it is worth noting that both of these phenomena would be expected to reduce the transmembrane flux relative to the prediction of a theory that neglects them. The topic of molecular diffusion through carbon nanotubes still has several areas in which progress can be made using molecular simulations, but we feel that the greatest opportunity (or need) in this area is for detailed experimental measurements. We reiterate an idea that we have presented elsewhere^{11,12} that performing experiments of gas mixture permeation through carbon nanotube membranes would reveal considerably more about the mechanisms underlying gas transport through these materials than experiments with single gases.

Acknowledgment. This work was partially supported by the National Science Foundation (CTS-0413027 and CTS-0406855). J.K.J. and D.S.S. are NETL Faculty Fellows. Helpful conversations with S. Bhatia and D. Nicholson are gratefully acknowledged. We thank F. Keil and S. Jakobtorweihen for helpful discussions and for sharing thermostat parameters for the (15,0) SWNT prior to publication.

References and Notes

- (1) Kärger, J.; Ruthven, D. *Diffusion in Zeolites and Other Microporous Materials*; John Wiley & Sons: New York, 1992.
- (2) Yang, R. T. *Gas separation by adsorption processes*; Butterworth: Boston, 1987.
- (3) Keil, F. J.; Krishna, R.; Coppens, M. O. *Rev. Chem. Eng.* **2000**, *16*, 71.
- (4) Merkel, T. C.; Freeman, B. D.; Spontak, R. J.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A. J. *Science* **2002**, *296*, 519.
- (5) Smit, B.; Krishna, R. *Chem. Eng. Sci.* **2003**, *58*, 557.
- (6) Freeman, B. *Macromolecules* **1999**, *32*, 165.
- (7) Skoulidas, A. I.; Ackerman, D. M.; Johnson, J. K.; Sholl, D. S. *Phys. Rev. Lett.* **2002**, *89*, 185901.
- (8) Ackerman, D. M.; Skoulidas, A. I.; Sholl, D. S.; Johnson, J. K. *Mol. Sim.* **2003**, *29*, 677.
- (9) Chen, H.; Sholl, D. S. *J. Am. Chem. Soc.* **2004**, *126*, 7778.
- (10) Bhatia, S. K.; Chen, H.; Sholl, D. S. *Mol. Simul.* **2005**, *31*, 643.
- (11) Skoulidas, A. I.; Sholl, D. S.; Johnson, J. K. *J. Chem. Phys.*, in press.
- (12) Chen, H.; Sholl, D. S. *J. Membrane Sci.*, in press.
- (13) Arya, G.; Chang, H.-C.; Maginn, E. J. *Mol. Simul.* **2003**, *29*, 697.
- (14) Duren, T.; Keil, F. J.; Seaton, N. A. *Mol. Phys.* **2002**, *100*, 3741.
- (15) Hinds, B. J.; Chopra, N.; Rantell, T.; Andrews, R.; Gavalas, V.; Bachas, L. G. *Science* **2003**, *303*, 62.
- (16) Sokhan, V. P.; Nicholson, D.; Quirke, N. *J. Chem. Phys.* **2002**, *117*, 8531.
- (17) Sokhan, V. P.; Nicholson, D.; Quirke, N. *J. Chem. Phys.* **2004**, *120*, 3855.
- (18) Supple, S.; Quirke, N. *Phys. Rev. Lett.* **2003**, *90*, 214501.
- (19) Wei, X.; Srivastava, S. *Phys. Rev. Lett.* **2003**, *91*, 235901.
- (20) Theodorou, D. N.; Snurr, R. Q.; Bell, A. T. Molecular Dynamics and diffusion in microporous materials. In *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Eds.; Pergamon Press: New York, 1996; Vol. 7; p 507.
- (21) Sholl, D. S. *Ind. Eng. Chem. Res.* **2000**, *39*, 3737.
- (22) Cussler, E. L. *Multicomponent Diffusion*; Elsevier: Amsterdam, 1976.
- (23) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.
- (24) Greenfield, M. L.; Theodorou, D. N. *Macromolecules* **2001**, *34*, 8541.
- (25) Skoulidas, A. I.; Sholl, D. S. *J. Phys. Chem. A* **2003**, *107*, 10132.
- (26) Chong, S.-S.; Jobic, H.; Plazanet, M.; Sholl, D. S. *Chem. Phys. Lett.* **2005**, *408*, 157.
- (27) Skoulidas, A. I. *J. Am. Chem. Soc.* **2004**, *126*, 1356.
- (28) Skoulidas, A. I.; Sholl, D. S. *J. Phys. Chem. B* **2005**, *109*, 15760.
- (29) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188.
- (30) Kalra, A.; Garde, S.; Hummer, G. *Proc. Nat. Acad. Sci. U.S.A.* **2003**, *100*, 10175.
- (31) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. *Nature* **2005**, *438*, 44.
- (32) Krishna, R.; van Baten, J. M. *Ind. Eng. Chem. Res.*, in press.
- (33) Mao, Z. G.; Sinnott, S. B. *J. Phys. Chem. B* **2000**, *104*, 4618.
- (34) Mao, Z. G.; Sinnott, S. B. *J. Phys. Chem. B* **2001**, *105*, 6916.
- (35) Jakobtorweihen, S.; Verbeek, M. G.; Lowe, C. P.; Keil, F. J.; Smit, B. *Phys. Rev. Lett.* **2005**, *95*, 044501.
- (36) Jakobtorweihen, S.; Lowe, C. P.; Keil, F. J.; Smit, B. *J. Chem. Phys.*, submitted.
- (37) Skoulidas, A. I.; Sholl, D. S. *J. Phys. Chem. B* **2001**, *105*, 3151.
- (38) Skoulidas, A. I.; Sholl, D. S. *J. Phys. Chem. B* **2002**, *106*, 5058.
- (39) Chen, H.; Sholl, D. S. *Langmuir*, in press.
- (40) Mingo, N.; Broido, D. A. *Phys. Rev. Lett.* **2005**, *95*, 096105.
- (41) Jobic, H.; Karger, J.; Bee, M. *Phys. Rev. Lett.* **1999**, *82*, 4260.
- (42) Papadopoulos, G. K.; Jobic, H.; Theodorou, D. N. *J. Phys. Chem. B* **2004**, *108*, 12748.
- (43) Jobic, H.; Skoulidas, A.; Sholl, D. S. *J. Phys. Chem. B* **2004**, *108*, 10613.
- (44) Majumder, M.; Chopra, N.; Hinds, B. J. *J. Am. Chem. Soc.* **2005**, *127*, 9062.
- (45) Newsome, D. A.; Sholl, D. S. *J. Phys. Chem. B* **2005**, *109*, 7237.
- (46) Holt, J. K.; Noy, A.; Huser, T.; Eaglesham, D.; Bakajin, O. *Nano Lett.* **2004**, *4*, 2245.
- (47) Roth, M. W.; Mesentseva, J. *Mol. Simul.* **2004**, *30*, 661.