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Rapid Diffusion of CH_4/H_2 Mixtures in Single-Walled Carbon Nanotubes

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Adsorption and transport of molecules inside the pores of single-walled carbon nanotubes (SWNTs) have received considerable attention in recent years.[1−8] One phenomenon where SWNTs have been predicted to differ dramatically from other known nanoporous materials is the macroscopic diffusion rates of adsorbed gases. Molecular dynamics (MD) calculations by Skoulidas et al. indicate that the macroscopic diffusivities of CH_4, H_2, Ar, and Ne in defect-free SWNTs are orders of magnitude higher than in any other nanoporous material, and, equally surprisingly, somewhat faster than diffusion in the gas phase.[5,9] These results have recently been corroborated by simulations by Sokhan et al. of N_2 diffusion in SWNTs.[10] Extremely fast diffusion of 40 monomer polyethylene chains in SWNTs has recently been reported by Wei et al.[7] The rapid macroscopic diffusion of adsorbed molecules in SWNTs has important practical implications for using SWNTs in gas-separation membranes, since the net flux through such membranes is strongly influenced by diffusion.[11,12] Recent experimental studies of membranes composed of aligned multiwalled nanotubes reported gas fluxes consistent with rapid diffusion rates for permeation of single-component gases.[13]

There have been a number of simulation studies of gas transport in SWNTs that have reported diffusion coefficients orders of magnitude lower than those in the work cited above.[14−16] None of these studies contradict the predictions of rapid macroscopic diffusion described above. A number of these studies examined only self-diffusion,[14,15] that is, the net motion of tagged particles. The diffusion coefficients governing self-diffusion and macroscopic diffusion in porous materials are fundamentally different quantities,[17] and Skoulidas et al. and Sokhan et al. have shown that at moderate and high pore loadings, these diffusion coefficients differ by orders of magnitude in SWNTs.[5,9,10] The work that has reported small diffusion coefficients for macroscopic diffusion is based on MD simulations with diffuse scattering conditions at the pore wall.[16] These simulations instantly decorrelate particle momenta upon collision with a pore wall, leading to slow diffusion. MD simulations that carefully examined adsorbate/pore collisions in nanotubes have found that diffuse scattering provides a very inaccurate description of the low friction that SWNTs present to adsorbed molecules.[18,19] As a result, simulations that use diffuse scattering strongly underestimate diffusion rates in carbon nanotubes.

The rapid diffusion discussed above has only been studied previously for gases adsorbed in SWNTs as pure components. The macroscopic transport properties of adsorbed mixtures can differ substantially from their pure component counterparts in nanoporous materials, but in general, the connection between the two is poorly understood.[20,21] We know of only one study of the macroscopic diffusion of gas mixtures in SWNTs,[16] but this study used diffuse scattering boundary conditions that, as described above, are unphysical. We report here the first study of macroscopic diffusion of a gas mixture in SWNTs that assesses the impact of rapid macroscopic diffusion of the pure components on the mixture properties.

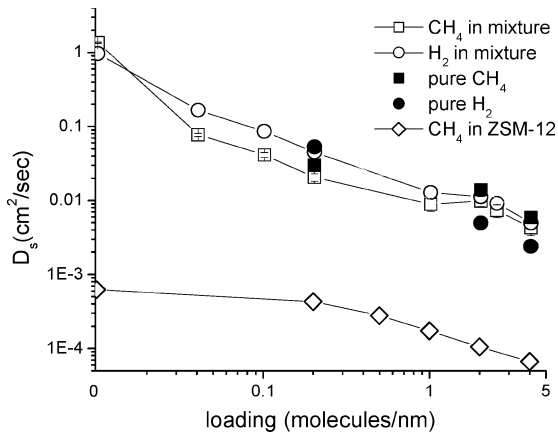

Figure 1. D_s for CH_4 and H_2 adsorbed in a (10,10) SWNT as equimolar mixtures (open squares and circles) or pure species (filled symbols) and for CH_4 in ZSM-12 (diamonds). Uncertainties are smaller than the symbols. Lines are to guide the eye.

We examined self-diffusion and macroscopic diffusion of equimolar CH_4/H_2 mixtures in (10,10) SWNTs at 298 K using equilibrium molecular dynamics (EMD). Methods for extracting self-diffusivities from EMD simulations are well-known.[17,21,22] EMD trajectories can simultaneously be analyzed to give the Onsager transport coefficients for macroscopic transport, L_{ij}.[23−27] In the Onsager formulation,[17,21] the macroscopic diffusive flux of species i, $\vec{J}_i$, is defined by $\vec{J}_i = -\sum_j L_{ij} \nabla \mu_j$. If the macroscopic flux is written using concentration gradients, then a matrix of Fickian diffusivities[17,21] is used in place of the Onsager coefficients: $\vec{J}_i = -\sum_j D_{ij} \nabla c_j$. The matrixes $[L]$ and $[D]$ can be related using the binary adsorption isotherm.[21,23] $[L]$ is a symmetric matrix, while $[D]$ is not. Our EMD simulations used the same methods as our earlier simulations of single-component gases in SWNTs.[5,9] These simulations model the nanotube structure as being rigid. Calculations with rigid and flexible nanotubes by Sokhan et al. have shown that nanotube flexibility plays only a minor role in determining the diffusivities of adsorbed species.[18] The interaction potential between H_2 and CH_4 was defined using the Lorentz−Berthelot combining rules. We performed 100 independent EMD trajectories, each of duration 15 ns, for each state point. The initial ballistic region (typically ∼4−6 ns of dynamics) in each ensemble of trajectories was discarded before calculating diffusivities.[5,9] Simulation details are described in the Supporting Information.

The self-diffusivities, D_s, of CH_4 and H_2 in equimolar adsorbed mixtures in (10,10) SWNTs from our EMD calculations are shown in Figure 1. For comparison, D_s for each species adsorbed as a pure component is also shown, as are the pure component

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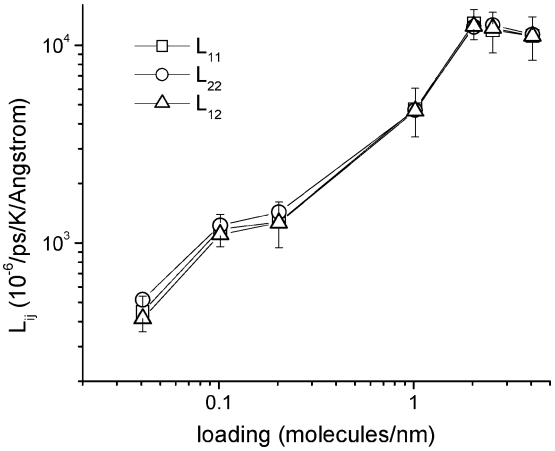

Figure 2. L_{11}, L_{22}, and L_{12} for equimolar CH_4/H_2 mixtures in a (10,10) SWNT. Subscript 1 (2) refers to CH_4 (H_2). Lines are to guide the eye.

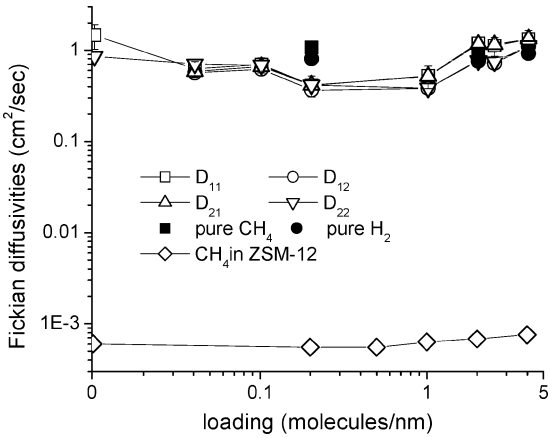

Figure 3. Fickian diffusivities, D_{ij}, for CH_4/H_2 equimolar mixtures in a (10,10) SWNT. Subscript 1 (2) refers to CH_4 (H_2). Pure species data for the SWNT (filled symbols) and in ZSM-12 (diamonds) are also shown.

diffusivities of CH_4 in ZSM-12, a typical silica zeolite with a one-dimensional pore.[26,27] The diffusivities in the mixture are very similar to those of the single-component adsorbates. Here and below, the concentration of adsorbed species is defined in terms of the number of molecules per unit length of the one-dimensional pore. In both materials, D_s decreases strongly as the pore loading is increased due to steric crowding.[26,27] Diffusion in the nanotube is much faster than in ZSM-12 at all pore loadings.

The Onsager coefficients, L_{ij}, for equimolar adsorbed mixtures of CH_4 and H_2 are shown in Figure 2, where here and below the subscript 1 (2) refers to CH_4 (H_2). The diagonal Onsager coefficients, L_{11} and L_{22}, are quite similar to each other. The Green−Kubo relations[23] defining the Onsager coefficients suggest that $L_{12} \cong \sqrt{L_{11}L_{22}}$ in one-dimensional pores, and we find that this expression is a very accurate description of our data. This relationship does *not* hold in three-dimensional pore networks, a fact we have confirmed by examining previous data for binary mixtures in silicalite.[20]

To determine the matrix of Fickian diffusivities, $[D]$, from our EMD data, we computed binary adsorption isotherms for CH_4/H_2 mixtures in (10,10) SWNTs using GCMC over a broad range of total pressures and gas-phase compositions. These adsorption data were well described by the same mixture isotherm as used in our previous work.[20] The fitted isotherm was used to generate the thermodynamic correction factors needed to relate $[D]$ to $[L]$.[20,21,23] The resulting Fickian diffusivities are shown in Figure 3. The Fickian diffusivities of pure CH_4 and pure H_2 in the same SWNT and pure CH_4 in ZSM-12 are also shown.

The principle observation to be made from Figure 3 is that the Fickian diffusivities of CH_4/H_2 mixtures in SWNTs, like their pure component counterparts, are extraordinarily large when compared with adsorbed gases in other nanoporous materials. Typical light gas diffusivities in silica zeolites are 3−4 orders of magnitude lower than the diffusivities reported in Figure 3, and diffusivities in polymers are even lower.[5] Our data suggest that diffusion inside SWNTs is much more closely related to diffusion in bulk gases than it is to diffusion in other nanoporous materials.

Figure 3 also shows that the off-diagonal Fickian diffusivities, D_{12} and D_{21}, are similar in size to the diagonal diffusivities. This observation also follows directly from the approximate relationship for L_{12} mentioned above and the definition of $[D]$. At a macroscopic level, this means net fluxes of one of the adsorbed species are very strongly effected by concentration gradients of the other species. Similar effects have been noted before in other nanoporous materials,[20] but the coupling between the species, as measured by the size of the off-diagonal diffusivities, appears to be stronger in SWNTs than has been observed previously. This strong coupling, and the observation that an accurate approximate relationship defining the coupling is available, may have interesting implications for possible applications of SWNTs in adsorption-based or membrane-based gas separations.

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Supporting Information Available: Simulation details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Wang, Q. Y.; Challa, S. R.; Sholl, D. S.; Johnson, J. K. *Phys. Rev. Lett.* **1999**, *82*, 956.
(2) Kalra, A.; Garde, S.; Hummer, G. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 10175.
(3) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188.
(4) Power, T. D.; Skoulidas, A. I.; Sholl, D. S. *J. Am. Chem. Soc.* **2003**, *124*, 1858.
(5) Skoulidas, A. I.; Ackerman, D. M.; Johnson, J. K.; Sholl, D. S. *Phys. Rev. Lett.* **2002**, *89*, 185901.
(6) Bhatia, S. K.; Nicholson, D. *Phys. Rev. Lett.* **2003**, *90*, 016105.
(7) Wei, X.; Srivastava, S. *Phys. Rev. Lett.* **2003**, *91*, 235901.
(8) Supple, S.; Quirke, N. *Phys. Rev. Lett.* **2003**, *90*, 214501.
(9) Ackerman, D. M.; Skoulidas, A. I.; Sholl, D. S.; Johnson, J. K. *Mol. Sim.* **2003**, *29*, 677.
(10) Sokhan, V. P.; Nicholson, D.; Quirke, N. *J. Chem. Phys.* **2003**, *120*, 3855.
(11) Freeman, B. *Macromolecules* **1999**, *32*, 165.
(12) Merkel, T. C. et al. *Science* **2002**, *296*, 519.
(13) Hinds, B. J. et al. *Science* **2003**, *303*, 62.
(14) Mao, Z. G.; Sinnott, S. B. *J. Phys. Chem. B* **2000**, *104*, 4618.
(15) Mao, Z. G.; Sinnott, S. B. *J. Phys. Chem. B* **2001**, *105*, 6916.
(16) Duren, T.; Keil, F. J.; Seaton, N. A. *Mol. Phys.* **2002**, *100*, 3741.
(17) Kärger, J.; Ruthven, D. *Diffusion in Zeolites and Other Microporous Materials*; John Wiley & Sons: New York, 1992.
(18) Sokhan, V. P.; Nicholson, D.; Quirke, N. *J. Chem. Phys.* **2002**, *117*, 8531.
(19) Arya, G.; Chang, H.-C.; Maginn, E. J. *Mol. Sim.* **2003**, *29*, 697.
(20) Skoulidas, A. I.; Sholl, D. S.; Krishna, R. *Langmuir* **2003**, *19*, 7977.
(21) Keil, F. J.; Krishna, R.; Coppens, M. O. *Rev. Chem. Eng.* **2000**, *16*, 71.
(22) Snurr, R. Q.; Kärger, J. *J. Phys. Chem. B* **1997**, *101*, 6469.
(23) 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.
(24) Sanborn, M. J.; Snurr, R. Q. *Sep. Purif. Technol.* **2000**, *20*, 1.
(25) Sanborn, M. J.; Snurr, R. Q. *AIChE Journal* **2001**, *47*, 2032.
(26) Skoulidas, A. I.; Sholl, D. S. *J. Phys. Chem. B* **2001**, *105*, 3151.
(27) Skoulidas, A. I.; Sholl, D. S. *J. Phys. Chem. B* **2002**, *106*, 5058.

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