Rapid Transport of Gases in Carbon Nanotubes

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We report atomistic simulations for both self- and transport diffusivities of light gases in carbon nanotubes and in two zeolites with comparable pore sizes. We find that transport rates in nanotubes are orders of magnitude faster than in the zeolites we have studied or in any microporous material for which experimental data are available. The exceptionally high transport rates in nanotubes are shown to be a result of the inherent smoothness of the nanotubes. We predict that carbon nanotube membranes will have fluxes that are orders of magnitude greater than crystalline zeolite membranes.

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Single walled carbon nanotubes (SWNTs) have many potential applications as molecular sieves, membranes, sensors, and ‘‘nanopipes’’ for the precise delivery of gases or liquids [1–7]. As with all microporous materials, molecular transport rates inside SWNTs may have a large impact on the usefulness of these materials [8]. If molecular transport through SWNTs is slow, their usefulness may be severely constrained. Here we show using atomistic simulations that diffusion rates of light gases inside defect-free SWNTs are orders of magnitude higher than in crystalline microporous zeolites with similar pore sizes. This observation applies to both the self-diffusion of individual molecules and to the transport diffusivity, the quantity that describes macroscopic diffusion. We compare gas fluxes through a model SWNT membrane with experimental and theoretical results for analogous zeolite membranes and find that SWNTs membranes may exhibit exceptionally high fluxes. Since nanotubes are predicted to have high selectivity for separating gases [7], our predictions indicate that a nanotube membrane would have both extremely high selectivity and flux, a long-standing goal of membrane technology [9].

We used atomistic simulations to predict the diffusive transport rates of CH_4 and H_2 in a range of SWNTs. Computer simulations of adsorption phenomena in SWNTs have proved to be a useful complement to experimental studies, providing insight into novel structures and dynamics of adsorbed H_2O, for example [1,10]. In this study we compare our SWNT results to analogous calculations for two siliceous zeolites: silicalite and ZSM-12. Transport of gases in silicalite has been widely studied both experimentally and with atomistic simulations, so this system aids us in estimating how closely our simulations mimic reality. ZSM-12 has roughly the same pore size as silicalite but has the same unidimensional pore topology as SWNTs, so it provides an excellent probe for the effect of pore dimensionality on transport. Zeolites such as these two are already widely used in many practical applications [8], so comparing the properties of SWNTs to them provides a practical benchmark. Each adsorbent was simulated as a rigid structure. Silicalite and ZSM-12 were fixed in their known crystallographic structures [11], the former in its orthorhombic form [12]. Both zeolites were modeled with chemical composition SiO_2. The pore diameters of these zeolites are approximately 0.8 nm (atom to atom) [11]. Two different nanotubes were considered, namely, the (10,10) and (6,6). The (10,10) and (6,6) nanotubes have diameters of 1.36 and 0.81 nm, respectively (atom to atom). Thus, the (6,6) nanotube has a very similar diameter to the zeolites considered here, while the (10,10) nanotube is slightly larger. We consider only adsorption inside the SWNTs, not adsorption in the interstices or the external surfaces of nanotube bundles. CH_4 and H_2 were each treated as spherical particles with pairwise Lennard-Jones interactions between adsorbates and the O (C) atoms in the zeolites (SWNTs). Potential parameters for the adsorbed species were taken from the literature [13,14]. Predicted adsorption isotherms and self-diffusivities for CH_4 using this model for silicalite are in quantitative agreement with experimental measurements [12,15]. The same potential parameters were used in our ZSM-12 simulations. The fluid-nanotube potentials were based on the potential parameters for fluid-graphite interactions, which reproduce the experimental CH_4- and H_2-graphite isotherms and isosteric heats [16,17].

We first computed the equilibrium adsorption isotherms for single-component H_2 and CH_4 in (10,10) SWNTs, silicalite, and ZSM-12 using standard grand canonical Monte Carlo techniques [18]. These three materials have similar volumetric adsorption capacities, as can be seen from the computed isotherms in Fig. 1. The adsorption of CH_4 in silicalite has been measured in multiple experiments and our computed isotherm is in quantitative agreement with experimental results [13,15].

Several different quantities are commonly used to describe single-component diffusion [8]. The net displacement of a single, tagged particle is described by

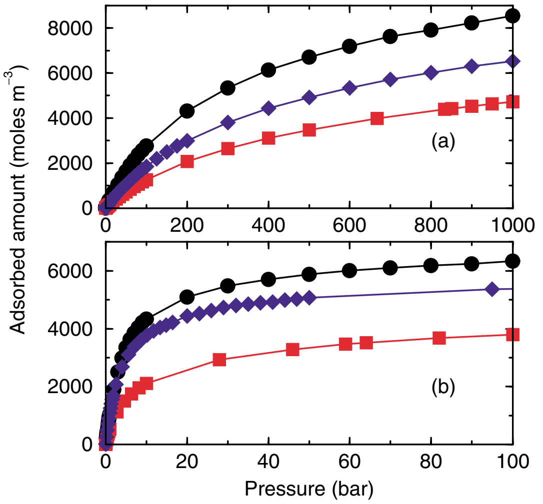

FIG. 1 (color online). Adsorption isotherms for hydrogen (a) and methane (b) in an array of (10,10) nanotubes (circles), silicalite (diamonds), and ZSM-12 (squares). The nanotubes are assumed to form a close-packed hexagonal structure. The zeolites are taken to be perfect crystals. Lines are to guide the eye.

the self-diffusivity, D_s. Specifically, the mean square displacement of a tagged particle in n dimensions satisfies the Einstein relation $\langle r^2(t) \rangle = 2nD_s t$ at long times. The transport diffusivity, D_t, defines the macroscopic flux of a diffusing species due to a concentration gradient expressed using Fick's law, $\mathbf{J} = -D_t \nabla c$. An important feature of diffusion in microporous materials is that both D_s and D_t are often strongly dependent on the diffusant concentration in the pores. Moreover, these two diffusivities are not equivalent except in the limit of dilute pore loadings [8]. For example, D_s of CH_4 in silicalite decreases strongly as the CH_4 concentration is increased, while D_t shows the opposite trend [12,19,20].

We used equilibrium molecular dynamics (EMD) to simultaneously determine D_s and D_t for adsorbed gases. Initial conditions were equilibrated using a combination of NVT-MC and NVT-MD [12,19]. After equilibration, NVT-MD trajectories were generated using a Nosé-Hoover thermostat. Test calculations using NVE-MD trajectories generated equivalent diffusivities. Self-diffusivities were calculated using the Einstein expression. All diffusivities reported below for SWNTs and ZSM-12 represent diffusion along the pore axis of the unidimensional pores. Diffusion in the 3D pore network of silicalite is anisotropic. Only the orientationally averaged diffusivity [12,20] is reported here. This diffusivity is the appropriate one for describing randomly oriented polycrystalline silicalite membranes [15].

Transport diffusivities were computed using the EMD method of Theodorou *et al.* [12,19,20]. EMD data for D_s and D_t were typically averaged over 15 independent simulations. Each simulation contained 80–480 molecules, depending on the pore loading being examined and followed the system's dynamics for 6.6–13.2 (2.3–4.6) ns for CH_4 (H_2) in zeolites and 13–65.8 (4.6–23) ns for CH_4 (H_2) in SWNTs. The length of time steps and equilibration methods were performed as described in Refs. [12,19]. Error bars were determined by averaging over the results from the independent simulations and computing the variance of the calculated average.

A comparison of H_2 and CH_4 self- and transport diffusivities in (10,10) nanotubes, silicalite, and ZSM-12 at room temperature is presented in Fig. 2. The range of pressures in Fig. 2 spans pore loadings from infinitely dilute to near saturation loadings. In the limit of dilute pore loadings, D_s in the SWNT is 3–4 orders of magnitude higher than in either zeolite. The difference in diffusion rates is due to the inherent smoothness of the SWNT. Simulations of fluids in model nanotubes in which artificial scattering is included during molecule-solid collisions result in diffusivities that are orders of magnitude lower than we observe in SWNTs [21]. Self-diffusivities in all three materials decrease with increasing loading. This drop, however, is much more pronounced in the nanotube than in the zeolites. This phenomenon occurs because molecule-molecule collisions introduce a mode of momentum decorrelation that dominates over the molecule-nanotube collisions due to the smoothness of the molecule-nanotube potential energy surface (PES). Mao and Sinnott have previously computed D_s for CH_4 at high pore loadings in SWNTs using different intermolecular potentials than in our work [22,23]. Good agreement is seen between these independent simulations. We also note that our computed D_s for CH_4 in silicalite is in quantitative agreement with experimental data [15]. In

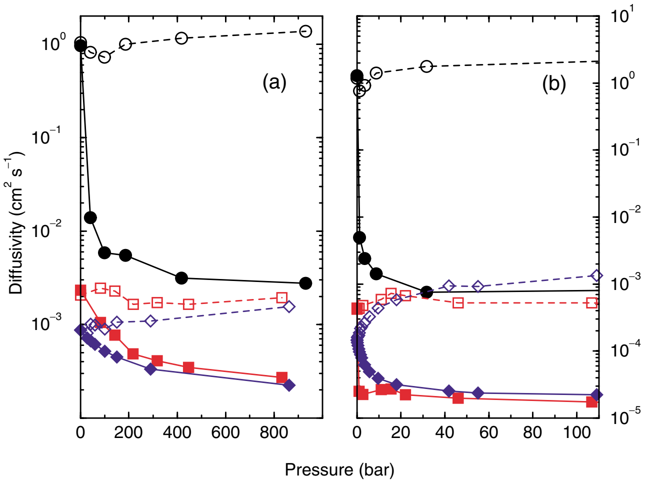

FIG. 2 (color online). Diffusivities for H_2 in (a) and CH_4 in (b). The filled symbols and full lines represent the self-diffusivities and the open symbols and dashed lines are values for the transport diffusivities. The adsorbents are (10,10) nanotubes (circles), ZSM-12 (squares), and silicalite (diamonds). Error bars are smaller than the symbol sizes. Lines are to guide the eye.

zeolites, molecule-solid collisions decorrelate momentum rapidly, even in the absence of molecule-molecule collisions, giving rise to both a much lower zero pressure diffusivity and a weaker dependence of D_s on loading. Even at high pressure, D_s in the nanotube is roughly an order of magnitude faster than in the zeolites. The dimensionality of the zeolite (silicalite is 3D, ZSM-12 is 1D) appears not to have much impact on the magnitude of D_s.

In stark contrast with self-diffusivities, transport diffusivities in (10,10) nanotubes are 3–4 orders of magnitude larger than in the two zeolites over the entire range of pressures we have examined. In SWNTs and ZSM-12 D_t is almost independent of pore loading. In silicalite D_t increases with increasing pore loading. The transport diffusion can be expressed as the sum of the self-diffusivity and terms accounting for velocity correlations between different molecules [19]. It is evident from our data that these velocity correlations are significantly larger in SWNTs than they are in silicalite or ZSM-12.

Transport and self-diffusivities for H_2 in (6,6) and (10,10) SWNTs are presented in Fig. 3. Diffusion in (6,6) nanotubes is faster than in (10,10) nanotubes. The higher curvature of the (6,6) nanotube leads to a smoother PES for H_2-wall interactions than for the (10,10) SWNT. (6,6) nanotubes and the zeolites considered here have essentially equal pore diameters, while (10,10) nanotubes are slightly larger. We have also examined the effect of nanotube chirality by comparing diffusion in (10,10) and (12,8) nanotubes. These two SWNTs, which are achiral and chiral, respectively, have virtually identical diameters. Diffusivities in these two nanotubes are almost the same, indicating that chirality is not important to light gas diffusion in SWNTs. This agrees with previous simulations of CH_4 self-diffusion in SWNTs[22].

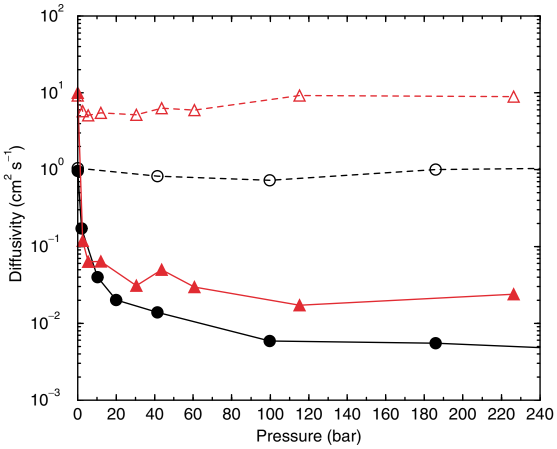

FIG. 3 (color online). Transport diffusivities (open symbols, dashed lines) and self-diffusivities (filled symbols, solid lines) of H_2 in (6,6) (triangles) and (10,10) (circles) nanotubes as a function of pressure. Error bars are roughly the same size as the symbols.

We determined the activation energies for CH_4 and H_2 diffusion to quantify the smoothness of each molecule-solid potential energy surface. In the zeolites, we computed D_s in the infinite dilution limit as a function of temperature and fitting the result to $D_s(T) = D_s^0 \exp(-E^{\mathrm{act}}/kT)$. Diffusion in SWNTs cannot accurately be described as an activated process, so we calculated E^{act}, the minimum energy required to move an adsorbed molecule along the pore, directly from the PES. For CH_4 in silicalite we find $E^{\mathrm{act}} = 4.16$ kJ/mol, in good agreement with experiments [15]. For CH_4 in ZSM-12 $E^{\mathrm{act}} = 4.31$ kJ/mol. For CH_4 in the (10,10) nanotube E^{act} is only 0.054 kJ/mol. The results for H_2 are similar; we find $E^{\mathrm{act}} = 2.62$, 3.09, and 0.066 kJ/mol in silicalite, ZSM-12, and the (10,10) nanotube, respectively. We emphasize that these values were obtained from fully atomistic models of each material. These dramatic differences in the smoothness of the molecule-solid PES lead to the huge differences between diffusion rates in the silica zeolites and SWNTs.

We emphasize that the rapid transport of adsorbed gases in SWNTs is not strongly dependent on the details of the adsorbate-nanotube interaction potentials because it is the lack of corrugation in the PES that allows rapid transport. If we were to repeat our calculations with modified interaction parameters, the predicted adsorption isotherms would change, since these are largely determined by the net energy gained upon adsorption, but the corrugation experienced once a particle was adsorbed would still be small. Indirect indications of the smoothness of the energy surfaces have been seen experimentally by showing that moving a long SWNT within a multiwalled nanotube required extremely small amounts of energy [24]. In addition to its implications for gas transport, the smoothness of carbon nanotubes has important implications for the possible sensitivity of these materials as selective sorbents [6]. We have considered only defect-free nanotubes in our calculations. The presence of defects in the nanotubes (heteroatoms, holes, etc.) may have a profound impact on molecular diffusion by adding corrugation to the molecule-solid PES.

We used our results to predict the steady state fluxes of methane through 10 μm thick membranes made of silicalite, ZSM-12, and (10,10) nanotubes. These fluxes can be predicted from D_t and the adsorption isotherms by assuming no transport resistances exist at membrane boundaries [15,25]. We considered ZSM-12 and nanotube membranes in which the pore direction is aligned across the membrane. The pore density of the nanotube membrane was taken to be that of the experimentally observed nanotube bundles [26]. In each case, the steady state CH_4 flux was determined for a constant pressure drop of 1.38 bars, a typical experimental value [15], across the membrane. Comparisons of this calculation with experiments using polycrystalline silicalite membranes showed excellent agreement between the

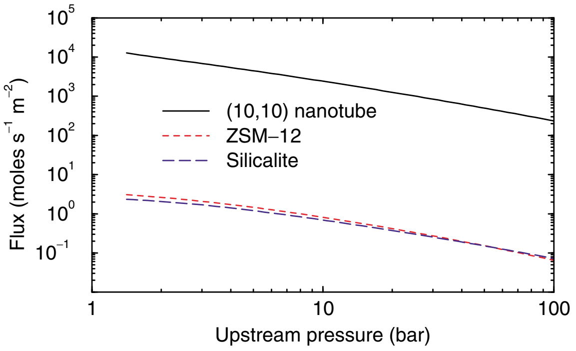

FIG. 4 (color online). Predicted flux of methane across a 10 μm thick membrane as a function of the upstream (inlet) pressure. The downstream (outlet) pressure is 1.38 bars lower than the upstream pressure.

model and experiment [15]. The steady state flux through each model membrane is summarized in Fig. 4. The fluxes through silicalite and ZSM-12 are similar. The most dramatic feature of Fig. 4 is the enormous enhancement in the flux through the nanotube membrane relative to the zeolite membranes. This is a direct result of the rapid diffusion of the adsorbed gas in the nanotube. The very large fluxes predicted for the nanotube membrane suggest that it should be possible to exploit nanotubes in novel membrane applications even in geometries where the packing of nanotubes is less dense than the one considered here.

It is helpful to compare our observed light gas diffusivities with other values known in bulk gases, liquids, and microporous materials at room temperature. Typical diffusivities in gases, liquids, and glassy polymers are 10^{-1}, 10^{-5}, and $10^{-10} - 10^{-9}$ cm^2 s^{-1}, respectively [27,28]. Diffusivities inside microporous solids are sensitive functions of the adsorbent structure. For example, the diffusivity of CH_4 is roughly 10^{-4} cm^2 s^{-1} in silicalite (see above) but only 4×10^{-11} cm^2 s^{-1} in zeolite 4A [8]. The diffusion of light gases in SWNTs is orders of magnitude faster than diffusion in any known microporous adsorbent, is considerably faster than diffusion in liquids, and in fact is the same order of magnitude for diffusion in gases.

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