The nanometer-scale size and hollow, cylindrical shape of carbon nanotubes suggests to many researchers that they may be used as molecular sieves, nanoscale test tubes, or hydraulic actuators or motors. They might also be used as ultrafiltration membranes (membranes with pores on the order of 1-100 nm) that are widely used in pharmaceutical industries. Such a nanotube membrane might function by routing molecules through the channels between the close-packed tubes in nanotube bundles or through the middle of chemically opened nanotubes.

Experimental and computational studies over the last two decades have shown that mass transfer through diffusive flow is dominant in nanometer-scale ideal pores and zeolites. Although carbon nanotubes and zeolites are both nanoporous materials, this does not necessarily mean that atomic and molecular diffusion in nanotubes will be the same as in zeolites. There are some important differences between the two in that nanotubes are composed of a single element and have a uniform, cylindrical channel structure, while zeolites are composed of multiple elements and have a non-uniform channel structure (Figure 1).

It has been established experimentally that compounds and elements with low surface tensions enter into opened carbon nanotubes if the tubes have diameters large enough to accommodate capillary motion. Much attention focused on filling nanotubes with hydrogen because using hydrogen as an energy source is a topic of intense interest to a variety of sectors including energy and transportation. However, the study of hydrogen storage in nanotubes has been controversial with contradictory experimental and theoretical results of uptake that is either much higher than or about the same as that of graphite.

In this article, we use computational methods to demonstrate the diffusive flow of organic molecules (CH₄ and C₆H₁₂), inorganic molecules (CO₂), and molecular mixtures (CH₄/C₂H₆, CH₄/n-C₄H₁₀, and CH₄/i-C₄H₁₀) through carbon nanotubes. The computational approach used is classical molecular dynamics (MD) simulations, where Newton’s equations of motion are numerically integrated to track the motion of the atoms with time. The forces on the atoms are calculated using methods that vary with distance: short-range C–C and C-H interactions are calculated using a reactive empirical bonding order hydrocarbon potential that realistically describes covalent bonding within both the molecules and the carbon nanotubes. This potential has been widely used in many simulations of carbon nanotubes. The long-range C-C and C-H interactions are characterized with Lennard-Jones (LJ) potentials. In the case of CO₂, the intramolecular bonds are held fixed and the atoms interact with each other and the nanotube walls via a combination of LJ and Coulombic interaction potentials.

The nanotubes considered by us vary in length between 80 Å and 150 Å and a range of nanotube diameters and helical structures are considered. The opened nanotubes are terminated with either C (in the form of truncated, open nanotubes with dangling bonds) or H atoms (that satisfy the truncated, open nanotubes). Both cases are considered to assess the effect of reactivity at the nanotube opening.
Nanotubes as Membranes, (cont.)

At the start of the simulations the molecules of interest are placed near the opening at one end (Figure 2). In some cases periodic boundary conditions are applied in the directions normal to the nanotube axis in order to confine the molecules in a specified volume near the nanotube opening while leaving motion in the direction of the nanotube axis free. These starting conditions therefore correspond to an external molecular pressure gradient along the length of the nanotube.

The simulations predict that the molecules enter into the nanotubes and diffuse down their length from areas of high to those of low density. The simulations are non-equilibrium, so the behavior of the first few molecules to enter the nanotube is not necessarily the same as the behavior of the diffusing molecules that have achieved a steady state environment. Figure 3 illustrates how the number of the CH$_4$ molecules entering and leaving a given nanotube reaches a steady state after about 60 ps. Prior to this, the number of molecules entering the nanotube is significantly larger than the number of molecules leaving the tube.

Diffusion varies with molecular size and shape and nanotube diameter. This is clearly shown in Tables I and II, which summarize the results for the diffusion of pure gases of CH$_4$ and C$_2$H$_6$ in nanotubes of various diameters. The results indicate that the CH$_4$ always follows normal-mode diffusion, where individual molecules can pass each other within the nanotube. In contrast, C$_2$H$_6$ diffuses by single-file mode in the smallest diameter nanotubes, where individual molecules cannot pass each other because of their relatively large size. As the nanotube diameter increases, these linear molecules switch to a mode that is intermediate between normal-mode and single-file diffusion. As the nanotube diameter increases further, the diffusion mode of the C$_2$H$_6$ transforms to normal-mode diffusion.

These results indicate that if the molecular structure is spherical, as it is in CH$_4$, the diffusion can be clearly distinguished as either normal-mode or single-file mode. However, if the molecular shape is highly asymmetrical, as is the case with C$_2$H$_6$, transition-mode diffusion can occur over short time scales. Transition mode diffusion occurs in nanotubes with diameters that are large enough for the molecules to pass each other if they are all perfectly aligned parallel to the nanotube axis, but not large enough to allow them to pass each other if some of them undergo small-angle rotational motion. For C$_2$H$_6$ this corresponds to nanotube diameters of about 0.8 – 1.4 nm.

However, this is not the case for C$_2$H$_6$ diffusion in nanotubes with diameters between 1.3 and 2.2 nm at low molecular densities. In these nanotubes, C$_2$H$_6$ molecules that enter the nanotube follow a spiral path around the circumference of the nanotube so that the paths followed by the molecules are strongly correlated to the helical structure of the specific nanotubes. It is thought that the driving force for this spiral diffusion path is that the interaction energy between C$_2$H$_6$ and the nanotube wall is maximized when the molecules line up with the C-C bonds in the nanotube wall. To maintain this high level of interaction, the molecules move forward by aligning with neighboring C-C bonds within the nanotube wall to yield the helical path. The spiral diffusion path becomes more pronounced as the curvature of the nanotube increases (the nanotube diameter decreases). When C$_2$H$_6$ diffusion on graphite is considered, the C-C bonds do not line up with the bonds in the graphite surface. This indicates that the nanotube curvature serves to strengthen the interactions between the C$_2$H$_6$ and the C-C bonds in graphite. However, if the curvature is too severe, as is the case for nanotubes smaller than 1.3 nm, no spiral motion is seen as the molecules are forced into the center of the nanotube. In the case of nanotubes with diameters greater than 2.2 nm, the path of molecular motion becomes random, destroying any tendency towards following a spiral path.

Whether or not the C$_2$H$_6$ molecules follow a spiral path depends greatly on molecular density, which is varied

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**Figure 2. Initial setup of molecules at one end of the nanotube prior to the start of the simulations.**

**Figure 3. Plot of number of CH$_4$ molecules entering and leaving a C-terminated (10,0) carbon nanotube over time. The molecules residing in the nanotube are the sum of all the molecules that have entered the nanotube up to that point in time minus the sum of all the molecules that have left the nanotube. The entering and leaving molecule curves represent the number of molecules that have entered or left the tube at the specified time only.**

**Table I. Diffusion mode and coefficient for CH$_4$ in nanotubes of various diameters.**

<table>
<thead>
<tr>
<th>Nanotube Diameter (nm)</th>
<th>Diffusion Mode</th>
<th>Diffusion Coefficient ($10^{-9}$ cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10.0)</td>
<td>Normal</td>
<td>3.91</td>
</tr>
<tr>
<td>(12.0)</td>
<td>Normal</td>
<td>2.94</td>
</tr>
<tr>
<td>(14.0)</td>
<td>Normal</td>
<td>1.05</td>
</tr>
<tr>
<td>(16.0)</td>
<td>Normal</td>
<td>0.832</td>
</tr>
<tr>
<td>(18.0)</td>
<td>Normal</td>
<td>0.425</td>
</tr>
<tr>
<td>(20.0)</td>
<td>Normal</td>
<td>0.164</td>
</tr>
</tbody>
</table>

**Table II. Diffusion mode and coefficients and mobilities for C$_2$H$_6$ in nanotubes of various diameters.**

<table>
<thead>
<tr>
<th>Nanotube Diameter (nm)</th>
<th>Diffusion Mode</th>
<th>Diffusion Coefficient ($10^{-9}$ cm$^2$/s)</th>
<th>Mobility ($10^{-4}$ cm$^2$/V-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(9.0)</td>
<td>Single-file</td>
<td>9.0 x 10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>(10.0)</td>
<td>Single-file</td>
<td>6.4 x 10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>(12.0)</td>
<td>Single-file</td>
<td>8.1 x 10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>(14.0)</td>
<td>Single-file</td>
<td>7.3 x 10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>(16.0)</td>
<td>Single-file</td>
<td>6.8 x 10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>(18.0)</td>
<td>Single-file</td>
<td>2.1 x 10$^{-9}$</td>
<td></td>
</tr>
</tbody>
</table>
in our study from 0.156 to 0.408 g/cm³. At low density almost all the molecules inside the nanotubes diffuse along a spiral path. At high density, the first three to eight molecules diffuse along the spiral path and the rest do not because the molecule-molecule interactions get stronger as the concentration of C₂H₆ in the nanotubes increases. This causes the C₂H₆-nanotube wall interactions to weaken enough that the C₂H₆ molecules no longer follow a spiral route.

When the nanotube diameters increase to 3.6 nm, in a (25,25) nanotube, no molecular diffusion is observed on the time scales of these classical MD simulations. It should be noted that 3.6 nm is the generally accepted cutoff for changes from diffusive motion to flow through other mechanisms, such as capillary motion or surface diffusion.

The effect of atomic termination at the nanotube opening is considered by comparing (reactive) C-atom termination with H-atom termination. At low densities of CH₄ (0.110 g/cm³), the molecules do not diffuse into H-atom terminated nanotubes as readily as into C-atom terminated nanotubes. However, as the density of CH₄ increases, the effect of atomic termination on the diffusion results decreases. For example, when the CH₄ density is 0.353 g/cm³ the diffusion coefficient for H-atom terminated nanotubes is about 2/3 of the value for diffusion into C-atom terminated nanotubes. In contrast, atomic termination has no significant effect on the diffusion of C₂H₆ at all the densities considered. This is because the smaller CH₄ molecules are more sensitive to the decreased attraction at the opening of the nanotube caused by H-atom termination while the large C₂H₆ molecules are not. No reactions occur between the molecules and the reactive C-atom terminated nanotube ends.

Moving from organic to inorganic molecular systems, preliminary studies have been completed on the diffusion of CO₂ in H-atom terminated (10,10) carbon nanotubes at 223 K. The results indicate that these molecules do not enter the nanotubes as readily as the organic molecules. Therefore, low molecular densities of CO₂ in the nanotube are seen in the simulations, as shown in Figure 4. Spiral diffusion is again predicted, with the C-O bond lining up with the C-C bonds in the nanotube walls. The reasons for this are similar to the reasons discussed above for the spiral diffusion of C₂H₆. It should be pointed out that the CO₂ molecules are able to get close to the nanotube walls and thus have interaction energies with the nanotube walls that are comparable to those of C₂H₆ and significantly larger (by a few tenths of an eV) than the interactions of the spherical CH₄ with the nanotube walls.

The CO₂ molecules do not leave the end of the nanotube at low molecular densities, but reverse their direction as they approach the open end. It is thought that this is due to the strong interactions between the molecules and the nanotube walls and is related to the density of the gas in the CNT. We are examining whether it can be removed by increasing the density of CO₂ at the mouth of the nanotube to drive CO₂ molecules into the nanotubes and push them out the other end.

The behavior of several molecular mixtures in carbon nanotubes is considered, including CH₄/C₂H₆, CH₄/n-C₂H₁₀, and CH₄/i-C₂H₁₀. These molecules can be classified according to their linearity in the following order:

more spherical CH₄ = iso-C₂H₁₀ < C₂H₆ < n-C₂H₁₀ more linear

For a given molecular mixture, as the diameters of the nanotubes decrease, the amount of separation of the molecular species increases. Furthermore, as the difference in the relative sizes of the molecules increases, the amount of separation of the molecular species also increases. In all cases, the molecular mixtures are characterized by large separation coefficients except for the CH₄/C₂H₆ system.

Both diffusion and adsorption are possible in the nanotubes for the larger n-C₂H₁₀ and iso-C₂H₁₀ molecules. For the very smallest nanotube diameters considered (0.7-1.1 nm) both n-C₂H₁₀ and iso-C₂H₁₀ go inside the nanotubes because they are too big for the nanotube opening, while the CH₄ moves along the nanotube by normal-mode diffusion. In the medium diameter nanotubes (1.1-1.5 nm), both n-C₂H₁₀ and iso-C₂H₁₀ enter the nanotubes but stay in the middle of the pore because there is not enough room for them to get close to the walls due to the relatively high curvature of the nanotube and their relatively large sizes. Therefore, they diffuse down the center of the pore in single-file mode.

In the largest diameter nanotubes considered (1.5-2.3 nm), both n-C₂H₁₀ and iso-C₂H₁₀ enter the nanotubes and have enough room to get close to the walls and physisorb. This behavior should be distinguished from the spiral diffusion behavior discussed above for C₂H₆ and CO₂. In this case absorption is characterized by the molecule getting close to the nanotube wall and staying there. It is possible that over larger time scales than those accessible in the classical MD simulations the C₂H₁₀ molecules would be

Figure 4. Snapshots of CO₂ molecules diffusing through a single, H-atom terminated (10,10) nanotube taken at 11 and 15 ps. A CO₂ molecule identified by a black colored carbon can be seen to follow a spiral path along the nanotube wall.
transported by surface diffusion. The n-C\textsubscript{4}H\textsubscript{10} adsorbs more strongly than iso-C\textsubscript{4}H\textsubscript{10} because its larger linearity allows the bonds in the molecule to align with the carbon-carbon bonds in the nanotube. Neither CH\textsubscript{4} nor iso-C\textsubscript{4}H\textsubscript{10} can get as close to the nanotube walls because of steric effects. Thus, in all three cases separation of the C\textsubscript{4}H\textsubscript{10}/CH\textsubscript{4} mixture occurs. However, the mechanisms are fundamentally different. These simulation results agree with the available experimental data that shows that n-C\textsubscript{4}H\textsubscript{10} absorbs to the walls of multi-walled nanotubes with diameters of about 30 nm.

Thus there are two factors that seem to most affect the diffusion behavior of molecules: one is the interaction between the molecules and the nanotube walls and the other is the interaction among the molecules themselves. The main driving force for diffusion is the first type of interaction listed. However, intermolecular interactions can have profound effects on the diffusion mechanism followed by a certain type of molecule. This is especially apparent in molecular mixtures where different types of molecules have different effects on each other during diffusion. This effect will increase as the size difference between different molecules increases.

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A recent experience highlighted just how uninformed some of the public is about coal and the role of coal in the world energy picture. I was helping to lead a field trip group of university faculty on a tour of a mine complex in Eastern Kentucky. The mine’s safety director was explaining the mining process, when a young assistant professor of Communications asked him to explain “what is coal.” It became clear that he was not looking for a scientific answer. He really had no idea what coal is. Perhaps we might expect this from a group of elementary school students, but it is both astounding and alarming that an educated adult living in Kentucky could be unaware of coal.

Of course, if he had been aware of coal, there is a good chance he would not have a favorable opinion of the resource. The media is fond of portraying the coal industry and coal-burning utilities as polluters of streams and air and spoilers of land. Even in Kentucky, which enjoys the lowest electricity costs in the United States thanks to 95 percent of its electricity being produced from the burning of coal, the local newspapers, at least in Lexington and Louisville, portray coal in less than flattering terms. Our poor press coverage does not stop at the local level. The Economist (2002) portrayed “CO2AL” as “Environmental enemy No. 1.” With all due respect, perhaps few of us would argue with many of the points presented in the latter editorial. The basic facts presented, in many cases, differ little from facts published on the pages of publications like Energeia. The counterbalance of scientific opinion, however, was no more present than it is when the popular press writes about coal.

The best information about coal. For many years through the early 1990’s, a monthly newspaper, the voice of the coal mining industry in part of the Appalachians, was so poorly edited, that it perpetuated the stereotype of the poorly-educated coal miner. Even the National Mining Association (USA), the successor of the National Coal Association, is not immune from conveying misinformation. In their “Fast Facts About Coal” (National Mining Association, 2002), they state (at least through March 2003) that “Coal is a combustible mineral formed from the remains of trees, ferns and other plants that existed and died during the time of the dinosaurs.” This is true for certain Cretaceous coals in Utah, for example, where dinosaur footprints are found in the roof of the coal, but geologists working in the Pennsylvanian coalfields of the eastern United States or in the Paleocene coals of Wyoming have reason to dispute this generality.

What can we do about coal’s poor image? It is not an easy task. When we encounter adults who do not know what coal is, much less that it is the source of over 50 percent of the electricity in the U.S., we begin to realize that this is a daunting assignment. Consumers in many states are given an option of buying their power from sources other than the local utility, including purchasing renewable energy. In their prospectus to potential consumers, one renewable energy company admits that “we cannot guarantee that 100% of our power is renewable 100% of the time.” That is quite evident when they are marketing power nationally based on a current capacity of 50 MW of wind-generated power. Consumers in Illinois and Pennsylvania, major coal-producing states, can contract for renewable energy, but, more than likely, their electricity will come from coal or nuclear generation, not from wind power in California. A balance of energy sources is desirable, but the public needs to be educated about the present reality and future prospects of all energy sources, coal included.

Where do we start? Fortunately, educational resources are available. As an example, the Kentucky Coal Council has developed their “www.coaleducation.org” internet site. While there is a bias towards Kentucky, the lesson plans for elementary through secondary grades have a more universal base, many being...
modeled on successful programs in other states. Other resources are available through the American Coal Foundation and the US Department of Energy. The place to start is in the schools. Without a balanced energy education in the school years, we cannot hope to produce adults capable of making intelligent energy choices, much less separating facts from opinion in the news media. As coal scientists, we need to offer assistance to schools. I know from local experience that curricula are crowded, but anything, from a day in the classroom to providing an opportunity for students to tour laboratory facilities, or even work in laboratories, may make a difference in educating the public about coal, in particular, and energy, in general. Without any effort, we are faced with a population with no appreciation of what is on the other side of the light switch. In the U.S. and many other countries, the other side of the light switch, now and for the near future, is coal.

Jim Hower may be contacted at: hower@caer.uky.edu. A version of Dr. Hower's editorial appeared in the International Journal of Coal Geology 52 (2002).