MOLECULAR SEPARATION IN CARBON NANOTUBE MATERIALS: PREDICTIONS FROM MOLECULAR DYNAMICS SIMULATIONS

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Introduction

Carbon nanotubes have been proposed as good materials for separation membranes because of their hollow, cylindrical shape and growth in ordered, close-packed bundles. They already have or are expected to have many industrial applications in adsorption, separation, and catalytic process involving multi-component fluids. We have therefore studied the manner in which molecular mixtures separate after diffusion into individual carbon nanotubes or nanotube bundles. The mixed systems considered in our study are methane/n-butane, methane/ isobutane, methane/ethane, nitrogen/ oxygen, nitrogen/carbon dioxide and oxygen/carbon dioxide.

Computational Details

The computational approach used is classical MD simulations, where Newton's equations of motion are numerically integrated to track the motion of the atoms. The forces on the atoms are calculated using empirical methods that vary with distance.[1] Short-range interactions are calculated using a well-known, many-body, reactive empirical bond-order hydrocarbon potential that realistically describes covalent bonding within both the organic molecules and the carbon nanotubes.[2] The long-range interactions are characterized with Lennard-Jones (LJ) potentials.[3]

At the beginning of all the simulations, the molecules are placed near one open end of the nanotube and the system is equilibrated at 300 K. During equilibration, 90% of the atoms in the system are placed in a thermostat. Following equilibration, all the atoms in the molecules are allowed to evolve with no constraints while the atoms in the nanotube walls continue to have Langevin frictional forces applied to them. Time steps of 0.25 fs are used and most simulations run for about 150 ps.

Results and Discussion

We have studied the manner in which molecular mixtures separate after diffusion into individual carbon nanotubes (as shown in Figure 1) or nanotube bundles. Some of these molecular mixtures separate in a well-defined manner within the nanotubes while others do not. Some results are shown in Figure 2. The mechanisms by which the molecules diffuse through the nanotubes are also determined and found to play an important role in the separation of some mixtures. For instance, molecular structure has a large effect on the separation and diffusion behavior of binary molecular systems in nanotubes. Both n-butane and isobutane separate well from methane through diffusion (see Figure 1). In addition, the

helical structure of the nanotube walls is predicted to have no effect on the separation of molecular mixtures, but the diameter of the nanotube has a large effect on the results. As the diameter of the nanotubes increases, the amount of separation between the molecules decreases. Changing the atomic termination at the carbon nanotube ends has little effect on the separation trends. The molecules have more difficulty diffusing into H-terminated nanotubes than C-terminated nanotubes. However the separation trends do not change with atomic termination. In nanotube bundles, the diffusion behavior and coefficients of binary molecular systems changed relative to the diffusion behavior in individual carbon nanotubes.

Conclusion

The diffusion behavior of different molecular mixtures in carbon nanotubes has been studied with MD simulations. The separation of binary mixtures as a result of diffusion is predicted and the manner in which these results depend on nanotube properties such as diameter and helical symmetry is reported. The simulations also indicate how the structure and size of the molecules in the mixtures influence the results.

References

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Figure 1: Snapshots from simulations of molecular separation of methane/n-butane system through open, (10,0) nanotubes.
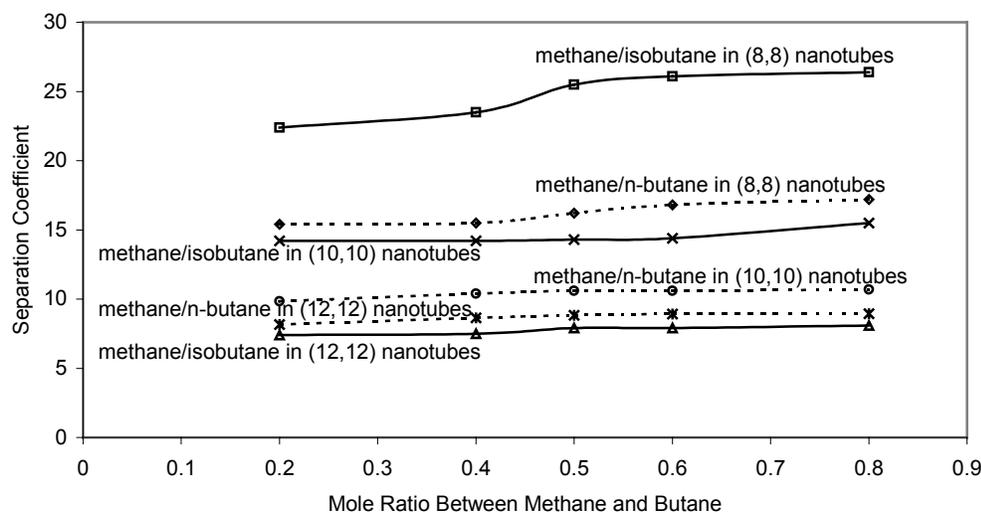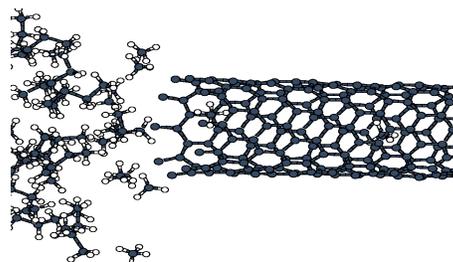

Figure 2: The separation coefficient vs the mole ratio of two types of molecules in (8,8), (10,10), and (12,12) nanotubes at 300 K.