Adsorption 2, 23–32 (1996)

Molecular Simulation of Binary Mixture Adsorption in Buckytubes and MCM-41

M.W. MADDOX, S.L. SOWERS AND K.E. GUBBINS
Cornell University, School of Chemical Engineering, Olin Hall, Ithaca, New York 14853

Abstract. MCM-41 and buckytubes are novel porous materials with controllable pore sizes and narrow pore size distributions. Buckytubes are carbon tubes with internal diameters in the range 1–5 nm. The structure of each tube is thought to be similar to one or more graphite sheets rolled up in a helical manner. MCM-41 is one member of a new family of highly uniform mesoporous silicate materials produced by Mobil, whose pore size can be accurately controlled in the range 1.5–10 nm. We present grand canonical Monte Carlo (GCMC) simulations of single fluid and binary mixture adsorption in a model buckytube, and nonlocal density functional theory (DFT) calculations of trace pollutant separation in a range of buckytubes and MCM-41 pores. Three adsorbed fluids are considered; methane, nitrogen and propane. The GCMC studies show that the more strongly adsorbed pure fluid is adsorbed preferentially from an equimolar binary mixture. Ideal adsorbed solution theory (IAST) is shown to give good qualitative agreement with GCMC when predicting binary mixture separations. The DFT results demonstrate the very large increases in trace pollutant separation that can be achieved by tuning the pore size, structure, temperature and pressure of the MCM-41 and buckytube adsorbent systems to their optimal values.

Keywords: GCMC, DFT, adsorption, MCM-41, buckytube, simulation

Introduction

Buckytubes and MCM-41 are novel porous materials with many potential applications in the fields of separation, heterogeneous catalysis and nanofabrication. A buckytube is a graphite tube consisting of one or more coaxial layers, first reported by Iijima (1991). Many different types have since been synthesized by a variety of methods (Ge and Sattler, 1993; Iijima and Ichihashi, 1993; Bethune et al., 1993; Howard et al., 1994). Much progress has been made in the separation and purification of the tangled mess of different buckytubes that are formed by the current synthetic techniques, and also in the removal of the hemispherical caps that often cover the ends of the tubes (Ebbesen et al., 1994; Tsang et al., 1993; Ajayan et al., 1993; Tsang et al., 1994). Buckytubes can now be made with internal diameters in the range 1–5 nm, and with any number of coaxial graphite layers from one to more than fifty. Most recently, Ajayan et al. (1994) have produced aligned arrays of monodisperse buckytubes, and Martin (1994) has reported a templating approach which could be used to produce monodisperse graphitic tubules of any desired diameter and wall thickness.

MCM-41 is one member of a new family of highly uniform mesoporous silicate materials produced by Mobil (Beck et al., 1992; Kresge et al., 1992). It has an hexagonal array of monodisperse pores, each of which is thought to be hexagonal or circular in cross section. The pore diameter can be accurately controlled in the range 1–10 nm. This class of materials is synthesized using a templating mechanism in which surfactant liquid crystal structures serve as organic templates.

These nanoscale materials are particularly interesting adsorbents because of the degree of control that can be exercised over their pore sizes, and the monodispersity of the pores within a given sample. This kind of synthetic control has the potential to lead to the production of 'designer adsorbents', whose properties are optimized for specific industrial separation processes.

Molecular simulation is a fast and efficient way to study the range of adjustable parameters in adsorption systems in order to optimize fluid separations. Here we present grand canonical Monte Carlo (GCMC) simulation results for single fluid adsorption of three major components of natural gas; methane, ethane and propane, in a model of a typical buckytube at 300 K. We also show GCMC results for the separation of two equimolar binary mixtures of these gases in the same buckytube and at the same temperature. Ideal adsorbed solution theory (IAST) provides a simple technique for calculating the separation of an adsorbed binary mixture using only the pure fluid adsorption isotherms, taken at the same temperature and on the same adsorbent (Myers and Prausnitz, 1965). The accuracy of this method is dependent on the validity of the assumption that the adsorbed phase behaves like an ideal solution. When it is applicable, IAST is a useful way to predict separations without running lengthy simulations or even lengthier experiments. Here we test the usefulness of this theory for the natural gas systems being studied.

The removal of trace pollutants from gas streams is a separation problem of major importance. In such a system, the amount of pollutant is often close to the limit of infinite dilution. The separation realized in practice is dependent on several parameters including the pressure of the bulk gas phase, the size, shape, and chemical composition of the pores comprising the adsorbent material, the bulk phase composition and the temperature. Testing the effects of all these parameters on a particular separation is a time-consuming process if done experimentally or by molecular simulation. Here we use a theoretical method, nonlocal density functional theory (DFT), to investigate the influence of a range of parameters on the separation of trace components from a simple binary mixture in buckytubes and MCM-41. This method has been shown to give results in agreement with GCMC simulations for the separation of simple binary mixtures near infinite dilution in confined systems (Sowers and Gubbins, 1995), but has the advantage of being much faster. It is therefore feasible to use this technique to cover a broad parameter range.

Methods

GCMC simulations are convenient for adsorption work because the grand canonical ensemble keeps the temperature, volume and chemical potential of the system fixed. When studying adsorption we are concerned with the equilibrium between a bulk fluid phase and an adsorbed phase, both at the same temperature and chemical potential. Thus in GCMC the chemical potential in the pore is fixed at a known value, and the corresponding bulk fluid pressure can be obtained from an equation of state. The simulation involves two perturbations: (a) molecular displacement, (b) trial insertion and deletion of molecules. The energy is recalculated following these trial moves, insertions and deletions, and they are accepted or rejected according to Monte Carlo recipes that are based on the laws of equilibrium statistical mechanics. The desired properties are obtained by averaging over the resulting chain of accepted configurations (Allen and Tildesley, 1987).

The nonlocal density functional theory used here is that of Kierlik and Rosinberg (1991), which follows the general formalism of other density functional theories (Evans, 1992). It is based on the usual separation of fluid-fluid interactions into attractive and repulsive contributions. The attractive contributions are treated in the mean-field approximation. The repulsive part of the intrinsic Helmholtz free energy is modeled by the free-energy functional of a reference hard-sphere fluid. The equivalent hard-sphere diameter is taken to be simply σ_{ff}, the Lennard-Jones diameter of fluid-fluid interactions. The application of density functional theory to adsorbed fluid systems involves the generation of a grand potential functional for the system, $\Omega[\{\rho_i\}]$, which includes a description of the fluid-fluid and fluid-wall interactions. The grand potential functional for this system is given by

$$\begin{aligned}\Omega[\{\rho_i\}] =& F^{\mathrm{hs}}[\{\rho_i\}] \\ &+ \frac{1}{2}\sum_{i,j}\iint d\mathbf{r}\, d\mathbf{r}'\rho_i(\mathbf{r})\rho_j(\mathbf{r}')\phi_{ij}^{\mathrm{attr}}(|\mathbf{r}-\mathbf{r}'|) \\ &- \sum_i \int d\mathbf{r}\rho_i(\mathbf{r})[\mu_i - \phi_i^{\mathrm{ext}}(\mathbf{r})] \qquad (1)\end{aligned}$$

where $F^{\mathrm{hs}}[\{\rho_i\}]$ is the free energy of a hard-sphere reference fluid, $\rho_i(\mathbf{r})$ is the number density of component i at position $\mathbf{r}$, $\phi_{ij}^{\mathrm{attr}}$ is the attractive part of the fluid-fluid potential, $\phi_i^{\mathrm{ext}}(\mathbf{r})$ is the external fluid-wall potential for a molecule of species i at $\mathbf{r}$, and μ_i is the chemical potential of component i. The ideal contribution to the repulsive part of the Helmholtz free energy is local, depending only on $\rho_i(\mathbf{r})$ at $\mathbf{r}$.

$$F_{\mathrm{hs}}^{\mathrm{ideal}}[\{\rho_i\}] = kT\sum_i \int d\mathbf{r}\rho_i(\mathbf{r})[\ln \rho_i(\mathbf{r}) - 1] \qquad (2)$$

For the excess contribution to the free energy functional of the reference hard-sphere fluid, Kierlik and

Rosinberg (1991) follow Percus (1988) and Rosenfeld (1990) in writing

$$F_{\mathrm{hs}}^{\mathrm{excess}}[\{\rho_i\}] = kT \int d\mathbf{r}\, \psi[\rho_a(\mathbf{r})] \qquad (3)$$

where $kT\psi$ is the excess part of the Helmholtz free energy density of the uniform hard-sphere fluid of density $\rho_a(\mathbf{r})$. A uniform density distribution of adsorbed particles equal to the bulk fluid density is initially assumed. The grand potential functional is at a minimum for the system at equilibrium, so that $\Omega[\{\rho_i\}]$ is first calculated for the initial configuration of adsorbed molecules, and then the density distribution is varied so as to minimize this functional. The resulting density distribution is used to calculate the amount of each fluid adsorbed at the given bulk fluid density, from which the selectivity of an adsorbed mixture can be found.

In the GCMC method, the fluid molecules are modeled as Lennard-Jones (LJ) spheres. The LJ interaction parameters, ε (potential well depth) and σ (interaction diameter) used in the GCMC simulations and DFT calculations are given in Table 1 (Hirschfelder et al., 1964). The subscript ii indicates an interaction between pairs of similar molecules. The LJ interaction parameters for pairs of dissimilar molecules, denoted ε_{ij} and σ_{ij}, are calculated from the pure fluid parameters using Lorentz-Berthelot mixing rules,

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \qquad (4)$$

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \qquad (5)$$

These are given in Table 2. All the fluid-fluid potentials in the GCMC simulations are cut and shifted at a cutoff radius of 5.0σ, at which point the LJ potential is almost zero.

Table 1. LJ interaction parameters for the single fluid potentials.

	CH_4	N_2	C_3H_8
σ_{ii} (nm)	0.3817	0.3750	0.5637
ε_{ii}/k(K)	148.2	95.2	242.0

Table 2. LJ interaction parameters for the fluid-fluid potentials.

	CH_4–N_2	CH_4–C_3H_8	N_2–C_3H_8
σ_{ij} (nm)	0.3784	0.4727	0.4694
ε_{ij}/k(K)	118.8	189.4	151.8

An interaction potential averaged over the surface structure of the adsorbent is used for the interaction between adsorbed fluid molecules and the wall of the buckytube or MCM-41 pore. This potential is calculated at each of 1000 points along the pore radius. At each point, the interaction between a fluid molecule adsorbed at that point, and every atom in the wall of the pore is calculated using LJ potentials for each individual atom-atom interaction. Linear interpolation is used within the GCMC and DFT computations in order to calculate the fluid-wall potential at points between those precalculated in this way. The wall of a buckytube is composed entirely of carbon atoms, but the wall of an MCM-41 pore contains oxygen and silicon atoms. As usual when modeling silicate materials, only the oxygen atoms are considered in the fluid-MCM-41 interaction. The process of averaging out the explicit surface structure of the adsorbent used here is analogous to that involved when calculating the 10-4-3 potential (Steele, 1974) for a planar graphite surface. The atomic positions of the carbon atoms in the model buckytube are calculated by a transformation of planar graphite atomic coordinates into a tubular structure. For the double buckytube, the two graphite layers are separated by 0.335 nm, the interlayer spacing of bulk graphite. Our atomistic models of two typical buckytubes are shown in Figs. 1 and 2. For MCM-41, our model is a first approximation to the actual structure, which has not yet been fully elucidated. It also involves a transformation of planar coordinates into a tubular structure, but this time the plane is a regular silicate surface. Additional silicate structure is built onto the single-layer tube to represent the MCM-41 structure further from the pore. Figure 3 shows our model of an MCM-41 pore. Although this model is clearly imperfect, it has been shown to reproduce an experimental nitrogen isotherm quite well (Maddox and Gubbins, 1994). The LJ parameters for the atom-atom fluid-wall interactions are calculated from the pure fluid-fluid parameters and the carbon-carbon and oxygen-oxygen parameters of the pore walls using Lorentz-Berthelot mixing rules. These values are shown in Table 3.

The separation of adsorbed mixtures is measured by a selectively defined by

$$S_2 = \frac{(x_2/x_1)}{(y_2/y_1)} \qquad (6)$$

where x_1 and x_2 are the mole fractions of fluids 1 and 2 in the adsorbed phase, and y_1 and y_2 are the mole fractions of fluids 1 and 2 in the bulk gas phase.

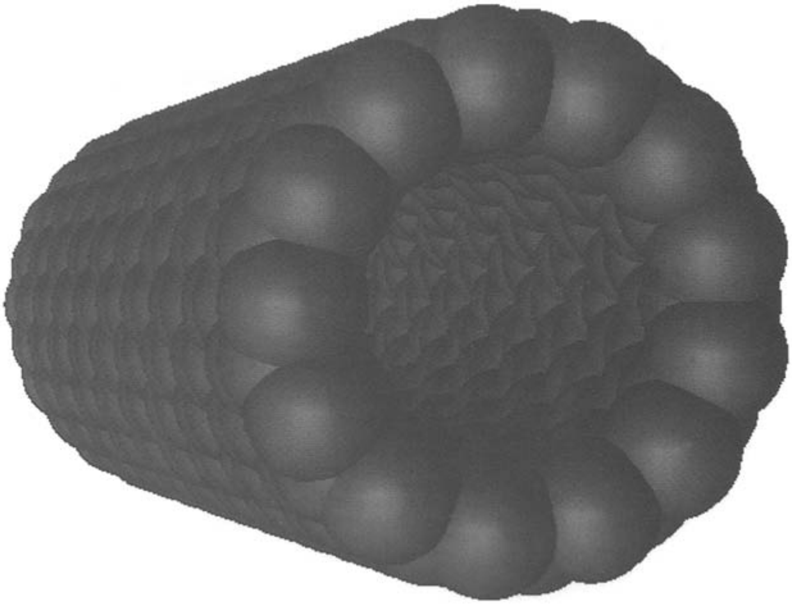

Figure 1. A short section of a 1.02 nm diameter single-buckytube.

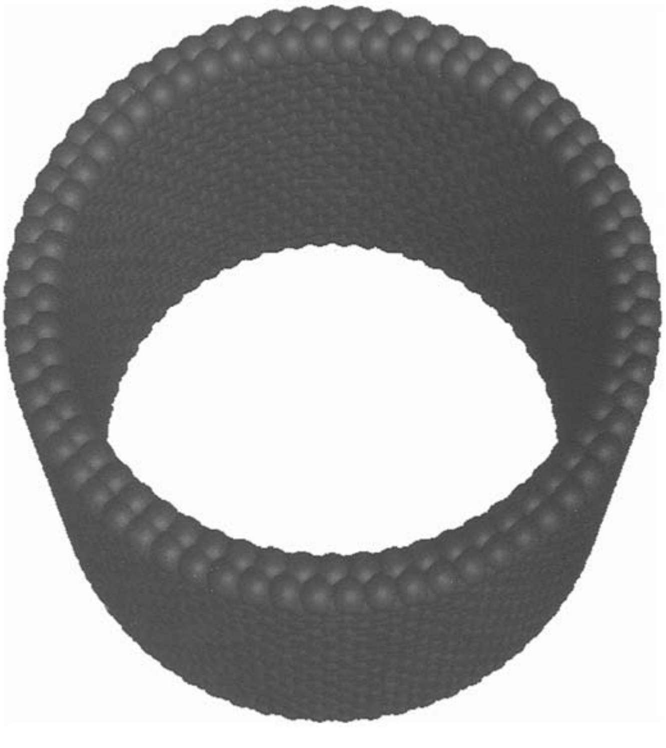

Figure 2. A short section of a 4.8 nm diameter double-buckytube.

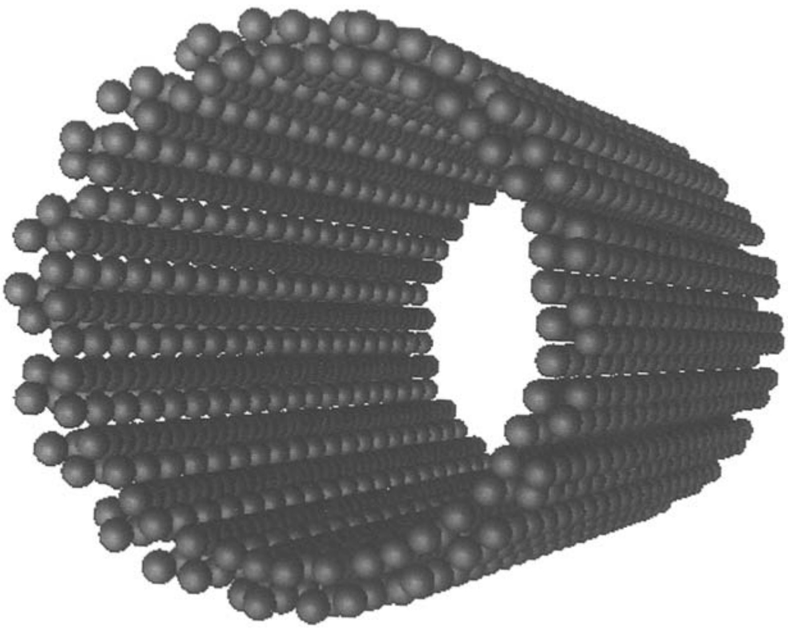

Figure 3. A short section of a 3.8 nm diameter MCM-41 pore. All the atoms shown are oxygen.

S_2 is therefore a measure of the adsorption selectivity for component 2 from a mixture of fluids 1 and 2. A selectivity of one represents no separation. A value greater than one shows that component 2 is preferentially adsorbed and a value less than one shows that component 1 is preferentially adsorbed. For a given mixture of fluids 1 and 2, we could equally well calculate S_1 rather than S_2 in which case $S_1 = S_2^{-1}$.

IAST theory provides a simple technique for calculating the compositions of the adsorbed and bulk gas phases for a mixture of gases, using only the adsorption isotherms for the pure gases, at the same temperature and on the same adsorbent (Myers and Prausnitz, 1965). The basis of the technique is the assumption that the adsorbed phase behaves like an ideal solution, the activity coefficients being equal to unity. In molecular terms, the intermolecular potentials for the various fluid-fluid pairs are assumed to be very similar. This approximation leads to an equation which is analogous to Raoult's law for liquid-vapor equilibria,

$$Py_i = P_i^0(\pi)x_i \tag{7}$$

where P is the total pressure of the gas phase, y_i is the mole fraction of component i in the gas phase, x_i is the mole fraction of i in the adsorbed phase, and $P_i^0(\pi)$ is the pure adsorbate gas pressure for component i at the temperature, T, and the spreading pressure, π, of the mixture. Spreading pressure is used in place of pressure in the adsorbed phase. For a binary mixture of gases, Eq. (7) leads to

$$P = P_1^0(\pi)x_1 + P_2^0(\pi)x_2 \tag{8}$$

A graphical approach can then be used to calculate the mixture adsorption equilibria and hence the selectivity from the pure component adsorption isotherms.

Discussion

The single fluid adsorption isotherms of methane, propane and nitrogen in a 4.8 nm diameter double-buckytube at 300 K, calculated by GCMC simulations, are shown in Fig. 4 (errors in the calculated adsorption are typically of the order ±1%). The amount of

Table 3. LJ interaction parameters for the fluid-wall potentials.

	CH_4-O	CH_4-C	N_2-O	N_2-C	C_3H_8-O	C_3H_8-C
σ_{ij} (nm)	0.3314	0.3609	0.3280	0.3575	0.4224	0.4519
$\varepsilon_{ij}/k(K)$	311.9	64.4	250.0	51.6	398.6	82.3

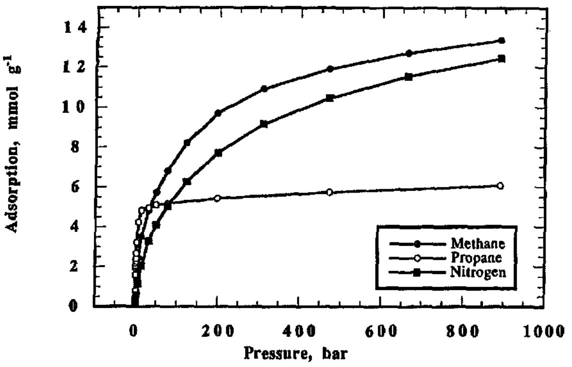

Figure 4. Adsorption isotherms for pure methane, nitrogen and propane in a 4.8 nm diameter double-buckytube at 300 K; GCMC simulations.

adsorption is initially measured as number of molecules per unit length of buckytube from the simulation. This is converted to mmol g^{-1} by dividing the number of moles of adsorbed molecules by the total mass of all the carbon atoms in the unit length of buckytube. Although earlier simulations showed the formation of several layers for nitrogen adsorbed in this buckytube at 77 K (Maddox and Gubbins, 1995), the increased mobility of the adsorbed molecules at 300 K prevents the formation of such discrete layers. Instead, these gases adsorb as simple Langmuir type isotherms, representative of type I adsorption in the IUPAC classification system (Sing et al., 1985), more usually associated with microporous adsorption. In each case the fluid is strongly attracted into the buckytube at low pressure due to the deep potential well in the fluid-wall interaction close to the buckytube wall. As the amount of adsorbed fluid increases, the most favorable sites, close to the wall of the tube, become occupied. Additional adsorbed molecules are forced to reside further from the wall where the interaction energy is less attractive. This causes the rate of adsorption to slow down and the slope of the adsorption isotherm to reduce. When the tube is filled with adsorbed molecules, further adsorption becomes very difficult, even at very high pressures, due to the strong repulsion an additional fluid molecule feels from the other fluid molecules in the filled tube. In this region the adsorption isotherm is almost flat; the amount of adsorption is at a maximum and changes very little with increasing bulk gas pressure. The maximum amount of adsorption is just over 13 mmol g^{-1} for methane, just under 13 mmol g^{-1} for nitrogen, and close to 6 mmol g^{-1} for propane. These differences are simply related to the size differences between the three types of molecule. This size effect is shown most clearly in the case of propane, which is considerably larger than either nitrogen or methane (the actual relative molecular volumes of methane, nitrogen and propane are approximately maintained in the spherical Lennard-Jones models used here). The initial slope of the propane isotherm (the Henry's Law region) is steeper than those of nitrogen or methane because of the stronger attractive interaction between propane and the buckytube wall.

Using the single fluid results described above, IAST is used to predict the selectivities of equimolar bulk gas mixtures of methane/nitrogen and methane/propane in the same 4.8 nm double-buckytube at 300 K. GCMC simulations were performed for the same mixtures for comparison. Figures 5 and 6 show the selectivities

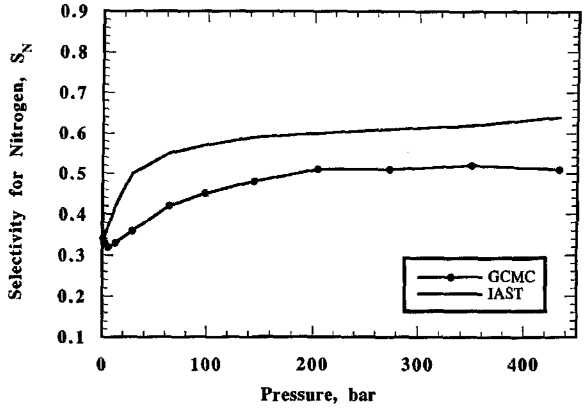

Figure 5. Selective adsorption of nitrogen from an equimolar methane/nitrogen mixture by a 4.8 nm diameter double-buckytube at 300 K; GCMC simulations and IAST.

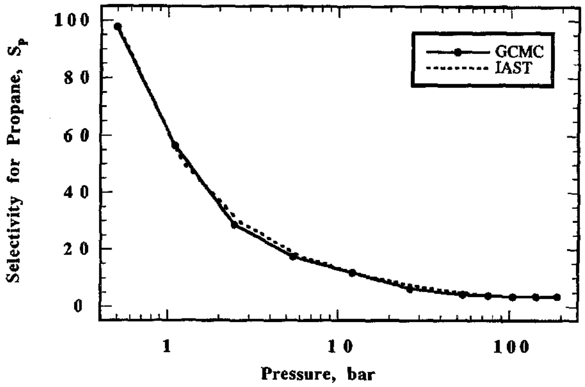

Figure 6. Selective adsorption of propane from an equimolar methane/propane mixture by a 4.8 nm diameter double-buckytube at 300 K; GCMC simulations and IAST.

from IAST and GCMC for these equimolar mixtures. The selectivity predicted by IAST and GCMC for nitrogen in the methane/nitrogen mixture is less than one for the whole pressure range, showing that methane is preferentially adsorbed from the equimolar bulk gas mixture. The selectivity for nitrogen decreases as the pressure is reduced, until a minimum value is reached, corresponding to a monolayer of molecules adsorbed on the pore wall. Below this pressure, the selectivity for nitrogen increases slightly. This minimum selectivity for nitrogen, corresponding to an optimum selectivity for methane, is seen on the GCMC curve at around 5 bar, in Fig. 5. No optimum selectivity is visible in Fig. 6 for the methane/propane system, but this is merely due to the very strong attractive forces between the propane molecules and the pore wall which cause the first monolayer to form at a pressure below the minimum pressure shown here. Therefore the optimum selectivity will occur at a pressure below 0.01 bar. The IAST results show reasonable qualitative agreement with GCMC for the methane/nitrogen mixture, and good agreement for the methane/propane mixture. Agreement between IAST and GCMC should be better at lower pressures because there are fewer interactions between the fluid molecules of each component and the mixture more closely approximates an ideal solution, even for adsorbed species that are quite dissimilar. At high pressures the adsorbed system can no longer be regarded as an ideal solution if there are any differences between the molecular interactions of different species. Since methane and nitrogen are quite similar in size, shape and intermolecular interaction, it is not surprising that the IAST results remain in fairly close agreement with GCMC, even at high pressure. It is however, slightly surprising that IAST gives such good results for the methane/propane mixture in the high pressure region. This is probably due in part to the use of Lennard-Jones spheres to model both adsorbates. IAST would therefore not be expected to work as well when predicting selectivities from experimental adsorption isotherms of these adsorbates. For the methane/propane mixture, IAST and GCMC both predict a selectivity greater than one for the whole pressure range. Again the degree of separation is greatest at low pressure. In both cases the fluid which has the stronger interaction with the buckytube wall is preferentially adsorbed. At low pressures fewer molecules are adsorbed, so those that are adsorbed will occupy the region close to the wall where the fluid-wall potential well is at its deepest and the difference between the interaction of different fluids with the wall is greatest. Hence the selectivity is larger. At higher pressures, more fluid molecules are adsorbed, many of which must reside further from the walls of the buckytube and experience much weaker fluid-wall forces. The difference in the fluid-wall interaction for the different fluids is smaller and the selectivity is therefore also smaller.

Figures 7–11 highlight the dramatic improvements that are possible in separation systems for trace pollutant removal by the careful tuning of a number of parameters. Temperature and pressure can be tuned in any adsorbent system, but the novel adsorbents MCM-41 and buckytubes also allow the pore size and structure to be varied in order to enhance separations, often to remarkable effect. Figure 7 shows nonlocal DFT results

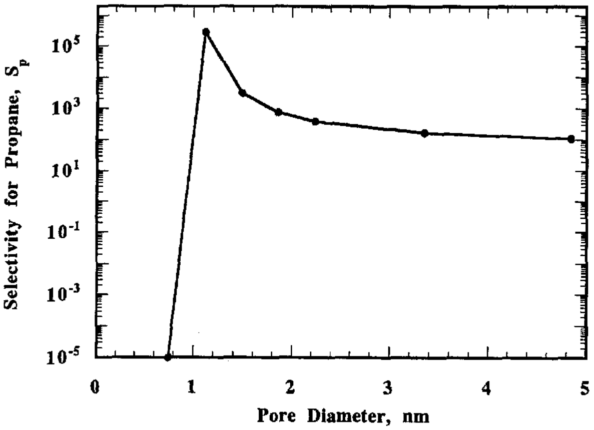

Figure 7. Selective adsorption of propane from a methane/propane mixture by a range of MCM-41 pores at 300 K, 0.27 bar and a bulk propane mole fraction of 1×10^{-7}; DFT results.

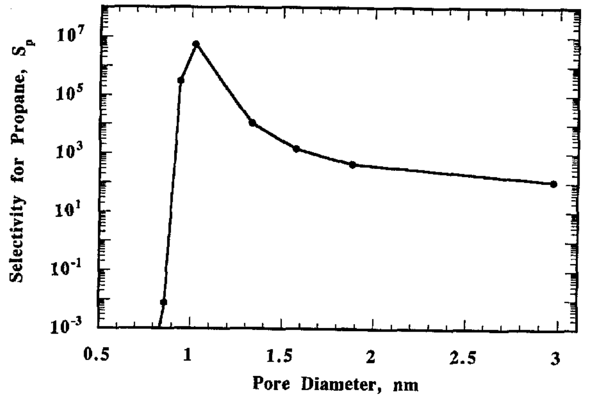

Figure 8. Selective adsorption of propane from a methane/propane mixture by a range of single-buckytubes at 300 K, 0.07 bar for a bulk propane mole fraction of 1×10^{-7}; DFT results.

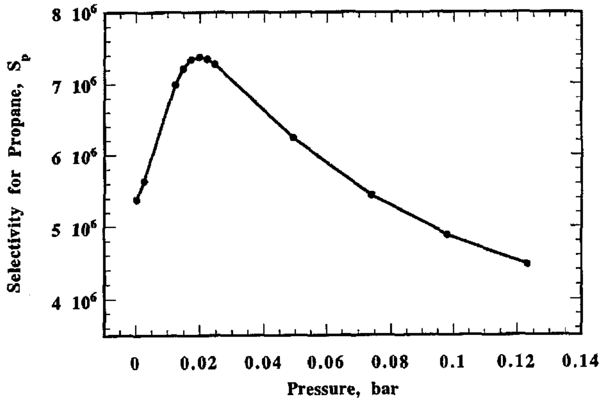

Figure 9. Selective adsorption of propane from a methane/propane mixture, for a range of pressures, by a 1.02 nm diameter single-buckytube at 300 K, and a bulk propane mole fraction of 1×10^{-7}; DFT results.

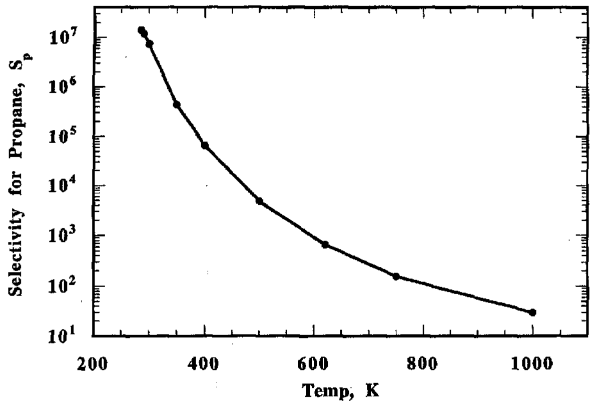

Figure 10. Selective adsorption of propane from a methane/propane mixture, for a range of temperatures, by a 1.02 nm diameter single-buckytube at 0.02 bar, for a bulk propane mole fraction of 1×10^{-7}; DFT results.

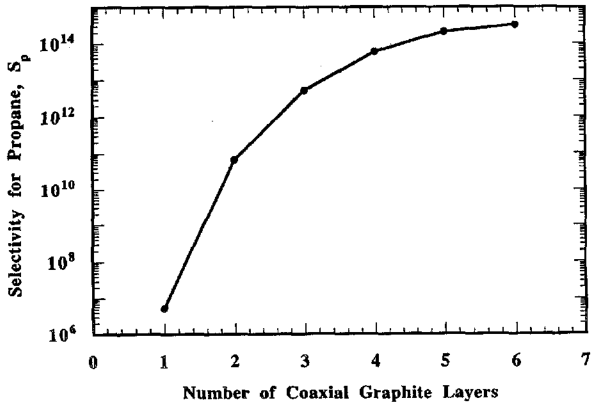

Figure 11. Selective adsorption of propane from a methane/propane mixture by a 1.02 nm diameter buckytube with varying numbers of coaxial layers, at 300 K, 5×10^{-12} bar, and a bulk propane mole fraction of 1×10^{-7}; DFT results.

for a methane/propane mixture in MCM-41 pores of different sizes. The bulk gas is methane with trace amounts of propane (1×10^{-7} mole %). The temperature is 300 K and the bulk mixture pressure is 0.27 bar. Points in the figure show the discrete range of pore diameters considered here. Lines are used to join the points since an almost continuous range of MCM-41 pore diameters is available in practice. At a pore diameter below 1 nm, the selectivity for propane is less than one, demonstrating a preference for methane adsorption in the pore despite the greater attraction between the MCM-41 pore wall and a propane molecule. This is simply a size-exclusion effect, the pore being too narrow to allow the larger propane molecules to enter. If we consider pore diameters slightly greater than the size of a propane molecule, propane is very strongly adsorbed in preference to methane, giving a very large selectivity of around 3×10^5. At larger pore sizes, propane is still adsorbed in great preference to methane, but the selectivity becomes smaller; for pore diameters in the range 3–5 nm it has a value of around 1×10^2, some three orders of magnitude less than the optimal separation. A similar behavior is observed in Fig. 8 where nonlocal DFT is used to calculate selectivities for the same bulk gas mixture at the same temperature and a slightly lower pressure, in single-walled buckytubes of varying diameters. Again, methane is preferentially adsorbed when the pore size is small enough to physically exclude the larger propane molecules, but propane adsorption is greatly favored once the buckytube is large enough to admit the propane molecules. Here the selectivity drops almost five orders of magnitude from the optimal diameter of around 1 nm to buckytubes greater than 3 nm in diameter. Under the same conditions of temperature, pressure, bulk phase mixture and pore size, the single-buckytube gives an optimum selectivity which is more than an order of magnitude greater than that achieved by MCM-41, because buckytubes adsorb the fluid molecules more strongly. Despite the larger ε parameters for the fluid-MCM-41 interactions, the density of carbon atoms in a buckytube is much greater than the density of oxygen atoms in an MCM-41 pore, so that the overall fluid-wall interaction is stronger in a buckytube.

Having established that a buckytube of around 1 nm in diameter will give an optimal selectivity for a bulk gas mixture of methane and 1×10^{-7} mole % propane, Figs. 9–11 show how the separation may be further improved by tuning the pressure, temperature, and the number of coaxial graphite layers of the buckytube. Figure 9 shows that finding the optimal pressure for the system, can increase the selectivity by up to 1.5 times over a pressure range of just 0.1 bar. Figure 10 indicates that large improvements in the separation can be achieved by carrying out the separation at a reduced temperature. Unlike the other parameters considered so far, it seems likely that there will be no maximum selectivity at a non-zero temperature, but that the separation will continue to improve toward absolute zero. Most dramatic of all is the effect on the selectivity of multiply layered buckytubes. In going from a single-walled tube to a buckytube of the same internal diameter, but comprising six coaxial layers, the selectivity increases by more than seven orders of magnitude from 6×10^6 to 3×10^{14}. This is simply explained by the large increase in the number of carbon atoms in the buckytube wall which contribute to the attractiveness of the fluid-wall potential. Each successive layer is made up of more carbon atoms than the last, but is also further from the adsorbed fluid. The latter effect predominates, slowing down the increase in the selectivity with each successive layer until each additional graphite layer is so far removed from the adsorbed fluid that it has little effect on the fluid-wall potential. In fact, although the addition of layers five and six improves the separation in an individual buckytube, the reduction in the specific surface area of an array of buckytubes due to this added carbon bulk could actually reduce the effective separation in a real, macroscopic system.

Conclusions

We have modeled the adsorption of three constituents of natural gas in a 4.8 nm double-buckytube at 300 K and shown that the adsorption isotherms are of IUPAC type I in each case. The initial slope of the isotherm (the Henry's Law region) is greatest for propane, then methane and then nitrogen. This is directly related to the different strengths of the fluid-wall interactions. The maximum amount of adsorption is greatest for methane, then nitrogen and then propane, because fewer larger molecules are needed to fill the buckytube. For equimolar bulk gas mixtures of methane/nitrogen and methane/propane adsorbing at 300 K in this buckytube, the component with the stronger fluid-wall interaction is preferentially adsorbed in each case; methane from the methane/nitrogen mixture and propane from the methane/propane mixture. In both systems the separation is greatest at low pressure. IAST shows good qualitative agreement with the simulation results for these mixtures.

Nonlocal DFT has been used to determine the separation of a trace quantity of propane from bulk methane by adsorption in MCM-41 and buckytubes, for a range of conditions. For both types of adsorbent, the separation is shown to be very sensitive to the pore size, and selectivities can be improved by several orders of magnitude by finding the optimal pore size. For MCM-41 and single-layered buckytubes, the optimal pore size for this bulk mixture is around 1 nm. At this diameter, the pore is just big enough to adsorb the large propane molecules. Such a single-layered buckytube with an internal diameter of 1 nm has already been prepared by Iijima and Ichihashi (1993). In addition to the pore size, the pressure, temperature, and fluid-wall interaction (the number of graphite layers in a buckytube), can also be tuned to improve the mixture separation by up to seven orders of magnitude.

Although we know of no experimental adsorption results for buckytube systems and only a few single fluid adsorption isotherms for MCM-41 (Branton et al., 1993; Franke et al., 1993), our simplified molecular simulations of these materials demonstrate their great potential as adsorbents for the separation of gas mixtures. The synthetic control of, and experimental research into these exciting new materials is currently in its infancy, but maturing fast. Within the next few years we anticipate many experimental studies of fluid adsorption in buckytubes and MCM-41. It is our hope that the work presented here will be helpful in directing such research towards systems that are more likely to be of practical use, and also in the interpretation of the experimental data. Future simulation work will seek to improve the current models by the inclusion of electrostatic forces and the use of more realistic atomistic models for larger fluid molecules. Recent MD simulations of MCM-41 (Feuston and Higgins, 1994), which have proposed a detailed atomistic model of this material, will also enable us to greatly improve our structural representation of an MCM-41 pore.

Nomenclature

ρ	density	mol m^{-3}
Ω	grand potential	J mol^{-1}
F^{hs}	free energy of hard sphere reference fluid	J mol^{-1}
$\mathbf{r}$	vector position of a fluid particle	m
ϕ^{attr}	attractive part of fluid-fluid potential	J mol^{-1}
ϕ^{ext}	external fluid-wall potential	J mol^{-1}
μ	chemical potential	J mol^{-1}

ρ_a	density of uniform hard-sphere fluid	mol m^{-3}
ψ	Helmholtz free energy	J mol^{-1}
ε	Lennard-Jones well depth	J mol^{-1}
k	Boltzmann constant	J K^{-1}
σ	Lennard-Jones molecular diameter	m
S_2	selectivity for component 2	
x_1	mole fraction of component 1 in the adsorbed gas phase	
y_1	mole fraction of component 1 in the bulk gas phase	
P	pressure	bar
π	spreading pressure	bar
T	temperature	K

Acknowledgments

We thank the Department of Energy for a grant (no. DE-FG02-88ER13974) in support of this work. Supercomputer time was provided under an NSF Metacenter grant (no. MCA93S011P). Finally we thank the Pittsburgh Supercomputer Center for the use of the C90 supercomputer.

References

Ajayan, P.M. and S. Iijima, "Capillarity-Induced Filling of Carbon Nanotubes," *Nature*, **361**, 333–334 (1993).

Ajayan, P.M., O. Stephan, C. Colliex, and D. Trauth, "Aligned Carbon Nanotube Arrays Formed by Cutting a Polymer Resin-Nanotube Composite," *Science*, **265**, 1212–1214 (1994).

Allen, M.P. and D.J. Tildesley, *Computer Simulation of Liquids*, Chapter 4, Clarendon Press, Oxford, 1987.

Beck, J.S., J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenker, "A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates," *J. Am. Chem. Soc.*, **114**, 10834–10843 (1992).

Bethune, D.S., C.H. Kiang, M.S. deVries, G. Gorman, R. Savoy, J. Vasquez, and R. Beyers, "Cobalt-Catalyzed Growth of Carbon Nanotubes with Single-Atomic-Layer Walls," *Nature*, **363**, 605–607 (1993).

Bezus, A.G., A.V. Kiselev, A.A. Lopatkin, and Pham Quang Du, "Molecular Statistical Calculation of the Thermodynamic Adsorption Characteristics of Zeolites using the Atom-Atom Approximation. Part 1-Adsorption of Methane by Zeolite NaX," *J. Chem. Soc. Faraday Trans.*, **74**, 367–379 (1978).

Branton, P.J., P.G. Hall, and K.S.W. Sing, "Physisorption of Nitrogen and Oxygen by MCM-41, a Model Mesoporous Adsorbent," *J. Chem. Soc. Chem. Commun.*, 1257–1258 (1993).

Ebbesen, T.W., P.M. Ajayan, H. Hiuri, and K. Tanigaki, "Purification of Nanotubes," *Nature*, **367**, 519 (1994).

Evans, R., *Inhomogeneous Fluids*, D. Henderson (Ed.), Dekker, New York, 1992.

Feuston, B.P. and J.B. Higgins, "Model Structures for MCM-41 Materials: A Molecular Dynamics Simulation," *J. Phys. Chem.*, **98**, 4459–4462 (1994).

Franke, O., G. Schulz-Ekloff, J. Rathousky, J. Starek, and A. Zukal, "Unusual Type of Adsorption Isotherm describing Capillary Condensation without Hysteresis," *J. Chem. Soc. Chem. Commun.*, 724–726 (1993).

Ge, M. and K. Sattler, "Vapor-Condensation Generation and STM Analysis of Fullerene Tubes," *Science*, **260**, 515–518 (1993).

Hirschfelder, J.O., C.F. Curtiss, and R.B. Bird, *Molecular Theory of Gases and Liquids*, 2nd Edition, J. Wiley and Sons, New York, 1964.

Howard, J.B., K.D. Chowdry, and J.B. Vander Sande, "Carbon Shells in Flames," *Nature*, **370**, 603 (1994).

Iijima, S., "Helical Microtubules of Graphitic Carbon," *Nature*, **354**, 56–58 (1991).

Iijima, S. and T. Ichihashi, "Single-Shell Carbon Nanotubes of 1-nm Diameter," *Nature*, **363**, 603–605 (1993).

Kierlik, E. and M.L. Rosinberg, "Density-Functional Theory for Inhomogeneous Solids: Adsorption of Binary Mixtures," *Phys. Rev. A*, **44**, 5025–5037 (1991).

Kresge, C.T., M.E. Leonowicz, W.J. Roth, J.C. Vartuli, and J.S. Beck, "Ordered Mesoporous Molecular Sieves Synthesized by a Liquid-Crystal Template Mechanism," *Nature*, **359**, 710–712 (1992).

Maddox, M.W. and K.E. Gubbins, "Molecular Simulation of Fluid Adsorption in Buckytubes and MCM-41," *Int. J. Thermophysics*, **15**, 1115–1123 (1994).

Maddox, M.W. and K.E. Gubbins, "Molecular Simulation of Fluid Adsorption in Buckytubes," *Langmuir*, **11**, 3988–3996 (1995).

Martin, C.R., "Nanomaterials: A Membrane-Based Synthetic Approach," *Science*, **266**, 1961–1966 (1994).

Myers, A.L. and J.M. Prausnitz, "Thermodynamics of Mixed-Gas Adsorption," *A.I.Ch.E. Journal*, **11**, 121–127 (1965).

Percus, J., "Free Energy Models for Nonuniform Classical Fluids," *J. Stat. Phys.*, **52**, 1157–1178 (1988).

Rosenfeld, Y., "Free-Energy Model for the Inhomogeneous Hard-Sphere Fluid: "Closure" relation between Generating Functionals for "Direct" and "Cavity" Distribution Functions," *J. Chem. Phys.*, **93**, 4305–4311 (1990).

Sing, K.S.W., D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Roquerol and T. Siemeneiewska, "Reporting Physisorption Data for Gas/Solid Systems," *Pure Appl. Chem.*, **57**, 603–619 (1985).

Sowers, S.L. and K.E. Gubbins, "Selective Removal of Trace Pollutants in Gaseous Streams by Adsorption in Micropores," submitted to *Langmuir* (1995).

Steele, W.A., *The Interaction of Gases with Solid Surfaces*, Pergamon, Oxford, 1974.

Tsang, S.C., P.J.F. Harris, and M.L.H. Green, "Thinning and Opening of Carbon Nanotubes by Oxidation Using Carbon Dioxide," *Nature*, **362**, 520–522 (1993).

Tsang, S.C., Y.K. Chen, P.J.F. Harris, and M.L.H. Green, "A Simple Chemical Method for Opening and Filling Carbon Nanotubes," *Nature*, **372**, 159–162 (1994).