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Exploiting Single-File Motion in One-Dimensional Nanoporous Materials for Hydrocarbon Separation

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ABSTRACT

The mobility of fluids adsorbed in nanoporous materials is a strong function of the size, shape, and dimensionality of the porous network. Nowhere is this dependence demonstrated more drastically than by fluids adsorbed in one-dimensional (cylinder-like) nanopores. It has been demonstrated theoretically, computationally, and experimentally that the mobility of a fluid adsorbed in one-dimensional nanopores varies with adsorbate size not only quantitatively (over several orders of magnitude) but also qualitatively.[1–4] When the pore size is small enough to prohibit passing of individual fluid molecules in the pore, the ordinary diffusion (where the mean square displacement is proportional to the observation time, and the proportionality constant is the diffusion coefficient) gives way to single-file motion (where the mean square displacement is proportional to the square root of the observation time, and the proportionality constant no longer has units of diffusivity). This difference in qualitative modes of motion results in

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a drastic quantitative difference in mobility; the single-file mode is much slower.

Using molecular dynamics simulations of methane and ethane in the one-dimensional molecular sieve, $AlPO_4$-5, this work demonstrates that the transition from ordinary diffusion to single-file motion can be exploited to effect a kinetic separation. In this case, methane molecules are small enough to pass each other in the pores of $AlPO_4$-5. The ethane molecules are too large to pass and undergo single-file motion. When a mixture of these two fluids is adsorbed in $AlPO_4$-5, the methane can still pass ethane and retains its fast, ordinary mode of diffusion. Thus, by careful selection of the adsorbent, we create an environment where these two fluids, with roughly the same bulk diffusivities, exhibit mobilities differing by several orders of magnitude.

This transport phenomenon has no bulk analog; it is a novel characteristic of fluids confined in nanoscale channels.

Key Words: Nanoporous materials; Single-file motion; Molecular dynamics; Adsorption; $AlPO_4$-5; Methane; Ethane.

1. INTRODUCTION

1.1. $AlPO_4$-5

There exists a class of zeolites and molecular sieves that contains a porous network of roughly cylindrical channels, which are arranged parallel to each other and, in the perfect crystal, never intersect. $AlPO_4$-5 is just such a molecular sieve. It contains roughly cylindrical pores created by rings of 12 oxygen, 6 phosphorus, and 6 aluminum atoms. These rings have a nominal diameter of 7.3 Å, although the cross-sectional area varies position along the channel axis, depending on whether one is at a ring or between rings.[1] Figure 1 shows a schematic of the $AlPO_4$-5 crystal structure. The crystal structure has been determined experimentally by X-ray diffraction.[2] We refer to a porous network of parallel cylindrical channels as one-dimensional. There is, of course, a radial dimension to the channel, but in terms of transport properties, there will only be a long-time nonzero mean square displacement of the adsorbate in the axial direction.

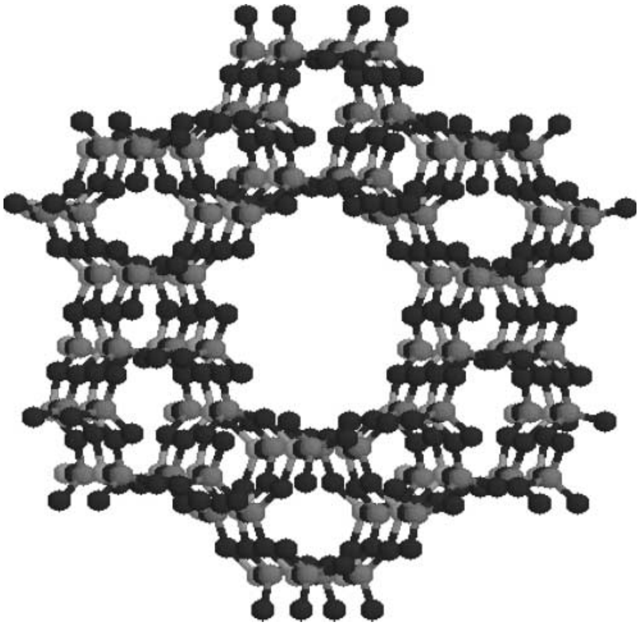

Figure 1. Schematic of the molecular sieve $AlPO_4$-5.

1.2. Unidirectional and Single-File Motion of Single-Component Fluids

When a single-component fluid is adsorbed in a one-dimensional porous network, two modes of motion are feasible. The first mode is ordinary, unidirectional diffusion, as predicted by Einstein's relation, where the mean square displacement is proportional to the observation time, t, in the long-time limit. The proportionality constant is twice the diffusion coefficient, D, which has units of length squared per time[3]:

$$\lim_{t\to\infty}\langle[x(\tau = t) - x(\tau = 0)]^2\rangle = 2Dt \qquad (1)$$

One physical assumption built into the diffusion equation, which yields this result, is that the individual atoms or molecules that make up the diffusing species be allowed to pass each other in the pore. See Fig. 2. If the channel becomes so small as to prohibit passing of the adsorbate molecules then the motion can no longer be described as ordinary diffusion. Instead, single-file motion is predicted by one-dimensional hard-rod (1DHR) theory.[4] In 1DHR

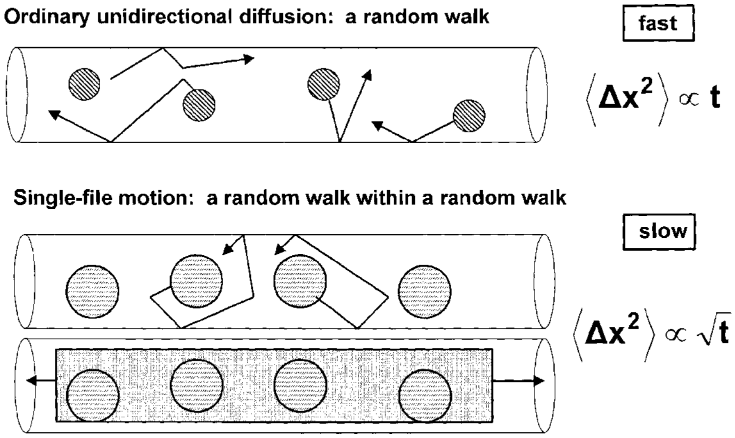

Figure 2. Schematic of modes of motion for a single-component fluid.

theory, the individual molecules undergo a constrained random walk. They are unable to exchange positions within the channel, and thus the ordered sequence of molecules is maintained. The entire chain of adsorbates then undergoes a second random walk. It is this random walk within a random walk that gives rise to a mean square displacement, which is proportional not to the observation time but to the square root of the observation time. 1DHR expresses this relation in a form obviously analogous to Einstein's relation:

$$\lim_{t\to\infty}\langle[x(\tau = t) - x(\tau = 0)]^2\rangle = 2\alpha t^{0.5} \tag{2}$$

The proportionality constant between the mean square displacement and the square root of the observation time is twice the single-file mobility factor, α. The single-file mobility factor has units of length squared per time to the one-half—to be contrasted with that of a diffusion coefficient. In this system, a diffusion coefficient is not defined. The single-file mobility factor has an analytical form that yields the dependence on the adsorbate one-dimensional number density, N, the adsorbate size, σ, and, the temperature, T, via an infinite dilution diffusivity, D_{id}:

$$\alpha = \frac{(1 - N\sigma)}{N}\left(\frac{D_{id}(\sigma, T)}{\pi}\right)^{0.5} \tag{3}$$

There is another, entirely equivalent formulation of the single-file mobility factor expressed in Eq. (2).[5] This alternate formulation expresses the single-file mobility given a well-defined lattice of adsorption sites where the single-file mobility is an explicit function of fractional loading, θ, lattice spacing, ℓ, and a mean time between successful moves between sites, τ. In the case of zeolites, where the adsorption sites do not have a well-defined maximum loading, nor regular spacing, parameters like θ, ℓ, and τ are difficult to estimate. Therefore, in this work, as in our previous work, we follow the less ambiguous formalism of 1DHR theory.

1.3. Review of Published Work

In addition to the theoretical studies of one-dimensional motion, single-file systems have been studied using computer simulations and experiments. Using pulse-field-gradient NMR, Nivarthi et al. demonstrated that methane, when adsorbed in the pores of $AlPO_4$-5, underwent ordinary unidirectional motion.[6] In this study, Nivarthi et al. were particularly careful to obtain large $AlPO_4$-5 crystals so that they could be sure that they were measuring purely intracrystalline diffusivity. The intracrystalline diffusivity they obtained was $3.0 \times 10^{-5}\ \mathrm{cm}^2/\mathrm{s}$ at a loading of 0.7 methane per unit cell and a temperature of 300°K. Subsequently, Gupta et al. used PFG-NMR to demonstrate that ethane in large crystals of $AlPO_4$-5 underwent single-file motion.[7] The single-file mobility, α, that Gupta obtained was $1.4 \times 10^{-7}\ \mathrm{cm}^2/\mathrm{s}^{0.5}$ at a loading of 0.2 ethane per unit cell and a temperature of 300°K.

It is not obvious on what basis one should compare the rapidity of the motion exhibited by methane and ethane because one is described by a diffusivity and the other by a single-file mobility. However, on a time basis as short as one second, we already see a mean square displacement that varies by a factor of over 200. This factor will increase rapidly as the observation time increases. The salient point is that single-file motion is a much slower mode of motion than ordinary unidirectional diffusion.

Concurrently with the PFG-NMR experiments of Gupta, Keffer et al. conducted molecular dynamics simulations of methane and ethane in $AlPO_4$-5.[8–9] In their work, they were able to provide plots of the mean square displacement with time, from which they could extract the exponents on the time dependence in Eqs. (1) and (2). They obtained precisely an exponent of 1.0 for methane and 0.5 for ethane, showing that methane indeed underwent ordinary diffusion and ethane single-file motion. Additionally, they were able to show that the density dependence of the single-file mobility factor, as predicted by 1DHR theory, was obeyed relatively well. They showed the same trend of a much slower single-file motion relative to ordinary diffusion.

Other workers have also conducted simulations and experiments of single-file motion in zeolites.[10,11] These results have also shown the single-file motion of ethane in $AlPO_4$-5. Additionally, they have examined the effects of motion in channels short enough to disrupt the single-file motion.

Nelson et al. have presented a theory that describes the self-diffusion of adsorbates in finite zeolitic systems. They contend that the transport of particles is Fickian at long times.[21] We are, however, studying systems at times shorter than the reported crossover time. Nelson et al. have also used kinetic Monte Carlo method to simulate tracer counter permeation. They present the conditions for different transport mechanisms to be exhibited based on anisotropy and thickness of their model membrane.[22] Kärger et al. have discussed the deviations from single-file diffusion in one-dimensional zeolitic systems.[23] Based on their analysis, they found that the PFG-NMR method was more accurate than QENS or the ZLC tracer exchange method in identifying single-file diffusion. Rödenback et al. have studied tracer exchange with single-file systems.[24] They provide a relationship between the mean intracrystalline residence time and the single-file chain length at various loadings.

Sholl and Fichthorn used smart Monte Carlo (SMC) to examined the motion of single-component and binary mixtures of ten fluids in $AlPO_4$-5.[12] They divide their single component results into “normal” for small components able to pass, and “single-file” for large species unable to pass. For their mixtures, they define three categories: “normal” (both ordinary diffusion), “dual-mode” (one single-file and one ordinary), and “single-file” (both single-file).

We have also studied the effect of modeling ethane as a two-center Lennard Jones molecule.[25] The molecular size that causes the transition from ordinary diffusion to single-file motion was found to be a function of the minimum dimension only.

1.4. Single-File Motion as a Separation Mechanism

Since it has been established in $AlPO_4$-5, (1) that methane undergoes ordinary diffusion, (2) that ethane undergoes single-file motion, and (3) that there is a drastic difference in the speed of these modes of motion, we now turn to exploiting this difference to effect a kinetic separation. In general, we can formulate four possible outcomes for the motion observed for a binary mixture of A and B adsorbed in a one-dimensional nanoporous network: Case (a): A can pass A. B can pass B. A can pass B. Case (b): A cannot pass A. B cannot pass B. A cannot pass B. Case (c): A cannot pass A. B can pass B. A cannot pass B. Case (d): A cannot pass A. B can pass B. A can pass B.

Since ethane does not pass ethane and methane passes methane, we should observe for the mixture the behavior in either case (c) or case (d), depending upon whether methane can pass ethane in the channel. See Fig. 3.

Whether methane can pass ethane in the channel is of crucial importance to whether the difference between ordinary diffusion and single-file motion can be exploited to effect a kinetic separation. The ability for mixed-pair passing should determine whether the methane undergoes single-file diffusion.

In case (c), if the methane cannot pass ethane, then it should not matter that the methane can pass other methane. Methane molecules will still undergo a pseudo-single-file type of motion, where clusters of methane are separated from other clusters of methane by ethane. The clusters undergo a single-file-type motion, based now on methane clusters and not on individual methane molecules. This will cause methane to exhibit a slow single-file motion, which will give it a mobility similar to that of ethane. Therefore, in case (c), since the mass transport properties are similar, the possibility of a highly effective kinetic separation is slim.

However, if the methane can pass ethane in the pores of $AlPO_4$-5 as in case (d), then methane should retain its high ordinary diffusive motion. One can speculate, based on the pure component results, that, if methane can pass ethane in $AlPO_4$-5, then a situation can be created where methane and ethane have mean square displacements separated by many orders of magnitude for any time scale longer than a second. This is a situation that is ideal for a kinetic separation.

This work investigates the potential to exploit the difference in single-file motion and ordinary unidirectional diffusion to effect a kinetic separation of a binary mixture.

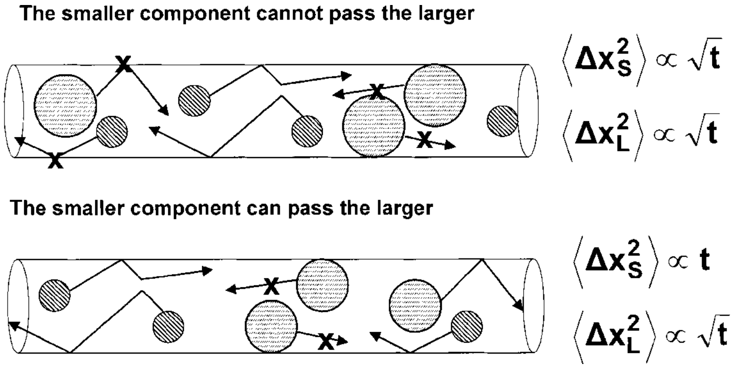

Figure 3. Schematic of modes of motion for a binary mixture.

2. METHODOLOGY

2.1. Potentials

The simulation techniques employed in this work were molecular dynamics simulations. The details of the simulation have been described previously.[9] The methane and ethane are modeled as single-center spheres. All interactions (Me–Me, Me–Et, Et–Et, Me–O, and Et–O) obey a Lennard-Jones 20-6 (LJ20-6) potential. The LJ20-6 potential was selected over the LJ12-6 in order to stiffen the adsorbates so as to prevent significant overlap of adsorbates. Otherwise, unrealistically large LJ ethane size parameters, σ_E, are required to prevent passing.[9]

The LJ20-6 species-i size parameter, σ_i, is the same as that for the LJ12-6, which has the effect of shifting the position of the energy minimum from $1.12\sigma_i$ for the LJ12-6 to $1.09\sigma_i$ for the LJ20-6. The LJ20-6 energy parameter, ε_i, is chosen such that the maximum i–i well-depth was the same as that for the LJ12-6 potential. This results in a slightly narrower potential well. The parameters for this potential are given in Table 1. The LJ12-6 methane and ethane parameters were obtained from the literature.[13] The methane–oxygen and ethane–oxygen parameters were obtained using the Kirkwood-Muller formulae.[9] The cutoff for the LJ potential was 12.0 Å.

We see that the choice of LJ20-6 over that of the LJ12-6 potential did not affect the diffusivity because at a loading of 1.0 LJ20-6 methane per unit cell $AlPO_4$-5, we find a diffusivity of $1.8 \times 10^{-4}\,cm^2/s$, which is expectedly slightly less than the values of $4.7 \times 10^{-4}\,cm^2/s$ at the lower loading of 0.7 LJ12-6 methane per unit cell, published previously (since diffusivity decreases with an increase in loading).[9]

The ethane and methane only interact with the oxygen of the $AlPO_4$-5 framework, following the suggestion of Beezus et al. that the oxygen contributes the most significant term to the potential.[14] The oxygen positions in the framework were taken from the X-ray crystallography data of Bennett et al.[2] The framework is rigid. While the assumptions of a single-center

Table 1. Lennard-Jones 20-6 parameters.

	Methane-methane	Methane-ethane	Ethane-ethane	Methane-oxygen	Ethane-oxygen
σ (Å)	3.882	4.941	5.000	3.083	4.832
ε (K)	137.0	177.5	230.0	141.1	49.7

methane and ethane as well as a rigid lattice are relatively unsophisticated models, we have established previously that these models can capture the fundamental physics governing the transition from ordinary diffusion to single-file motion.[9] However, we discuss some likely implications of these assumptions in the Conclusions section.

2.2. Simulation Techniques

The simulations used 256 adsorbate atoms (ethane + methane). The $AlPO_4$-5 unit cell contains 72 atoms. A $2 \times 2 \times 1$ (xyz) block of the unit cell creates the boundary for a central channel in the z-direction (as shown in Fig. 1). For 256 adsorbate atoms at a loading of 1.0 adsorbate atoms per unit-cell length, a block of $2 \times 2 \times 256 = 1024$ $AlPO_4$-5 unit cells (73,728 atoms) composed the simulation volume. This volume was bounded in all three dimensions by periodic images.

For each data point in the following graphs, the first 5,000 simulation steps were used for equilibration and discarded. Following equilibration, 1,000,000 simulation steps were conducted with a time step of 2.0 fs, yielding a total simulation time of 2 ns. Two ns has been shown to be sufficiently long to establish the long-time behavior of either ordinary diffusion (which is established in about 10 ps) or single-file motion (which takes much longer).[9] During data production, the Berendson thermostat was employed to maintain a constant temperature.[15] Newton's equations were integrated using the fifth-order Gear-predictor corrector.[16]

The simulations were conducted on a dual-processor SGI workstation, using the Message Passing Interface (MPI) library of communication subroutines. Each simulation took approximately 48 hours of CPU time.

The diffusivities reported in this paper were calculated using the Einstein relation.[3] During the simulation, positions were periodically saved. After the simulation was completed, mean square displacements were computed as a function of observation time. A least squares linear regression was performed for all observation times greater than 4.0 ps. (The extremely short time behavior is free-motion, where the mean square displacement scales as the square of the observation time.) This short time regime should not contribute to the long-time behavior used to determine the diffusivity. The standard deviations of the diffusivities were calculated from the coefficients of the linear regression.[17] The measure of fit of the least-squares regression to the mean square displacement-versus-time data was calculated to demonstrate the appropriateness of either the ordinary or single-file model.[18]

In cases where the adsorbates do not undergo ordinary motion but rather a single-file motion, the same data used to calculate the diffusivities can be used to perform a least squares linear regression for the single-file mobilities, except now the regression must be made on the mean square displacement versus the square root of the observation time. The mobilities, standard deviations, and measures of fit are then taken from the regression.

3. RESULTS AND DISCUSSION

3.1. Identifying Systems as Ordinary or Single-File Systems

In order to unambiguously discuss the differences between ordinary unidirectional diffusion and single-file motion, we must have some definite criteria to distinguish between them. The four criteria we have found to be most useful are:

- Shape of the mean square displacement vs. observation time (MSDvT) plot and measure of fit of Einstein's relation and 1DHR theory to the MSDvT plot
- Magnitude of diffusivities and mobilities obtained
- Rigorously numbering the atoms and noting the change in ordered sequence between initial and final configurations
- Watching movies of the simulation

Experimentally, with a technique like PFG-NMR, only the first two criteria are available. Each criterion has strengths and weaknesses. The first criterion, the shape of the MSDvT plot, is theoretically a rigorous criterion but is often practically somewhat difficult to gauge. For short observation times, with either simulation or experiment, the shape of MSDvT plot may not be clearly recognizable as either a linear or a square-root law with respect to observation time. One major reason for the ambiguity in the MSDvT plot is due to the fact that single-file motion takes more time to become established. Linear MSDvT plots for ordinary diffusion can be established in 10 ps. The square root behavior evolves more slowly and, from experience, is more subject to noise. A source of that noise, as we will see, especially in cases on the border of single-file motion, is that passing events may occur on a timescale of every 100–500 ps. In this case, in order to average out the passing events, a simulation of much longer duration, with many more atoms, is required.

Using least squares regression to obtain a measure of fit of the data to both the Einstein's relation and 1DHR theory is not always conclusive either, for the same reasons as given previously. In Fig. 4, we show the MSDvT plots for methane and ethane in order to demonstrate that pure methane in $AlPO_4$-5 undergoes ordinary unidirectional diffusion and pure ethane in $AlPO_4$-5 undergoes single-file motion. We show ethane with two different diameters for ethane, 5.0 Å and 6.0 Å. Ethane of both diameters undergoes single-file motion. The plots were obtained at $T = 298°K$ and a loading of 1.0 adsorbates per unit cell of $AlPO_4$-5. The most obvious conclusion from Fig. 4 is that single-file motion is a much slower mode of motion, as indicated by the smaller mean square displacement of ethane.

In the methane case, the MSDvT curve is visually linear. Both ethane curves closely obey a square-root dependence. Fitting both these curves to both Einstein's relation and 1DHR theory yields data shown in Table 2. As we expect for the pure component cases, the methane better fits Einstein's relation and ethane better fits 1DHR theory. However, the methane case also fits the single-file model better than the larger ethane. This is because single-file systems are more subject to noise, owing to the slower mode of motion, which

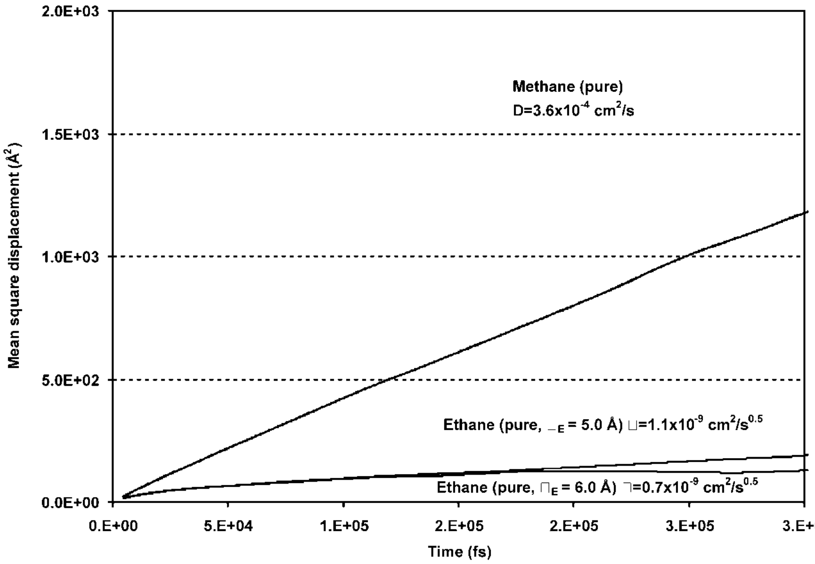

Figure 4. Pure-component mean square displacement versus observation time at $T = 298°K$, $\sigma_E = 5.0\,Å$ or $6.0\,Å$, $\sigma_M = 3.882\,Å$, $N_E + N_M = 1.0$ molecule/unit cell $AlPO_4$-5.

Table 2. Identifying ordinary and single-file motion.

	D (cm^2/s)	Fit (D)	α ($cm^2/s^{0.5}$)	Fit (α)	MSD in 0.5 ns ($Å^2$)	Passing
Pure						
Methane	1.8×10^{-4}	0.999	6.0×10^{-9}	0.961	2032	yes
Ethane (5 Å)	2.4×10^{-5}	0.912	5.5×10^{-10}	0.964	193	no
Ethane (6 Å)	1.4×10^{-5}	0.844	3.5×10^{-10}	0.942	116	no
Mixture						yes
Methane	7.5×10^{-5}	0.985	1.8×10^{-9}	0.982	739	yes
Ethane (5 Å)	2.3×10^{-5}	0.918	6.0×10^{-10}	0.986	161	no
Mixture						no
Methane	4.7×10^{-5}	0.959	1.2×10^{-9}	.920	590	yes
Ethane (6 Å)	3.2×10^{-5}	0.924	7.5×10^{-10}	.905	372	no

allows poorer averaging of low-frequency events during the simulation. In some simulations, the noise in the data can make the prediction of these fits unreliable. The noise could be reduced by running with much larger systems, as was done previously,[9] but this computational expense is unnecessary, since we have other criteria.

The second criterion, available in both experiment and simulation, is the magnitude of the mean square displacement (MSD) in the observation time. The pure methane MSD is 10–20 times larger than the ethane MSD. If we postulate, that we have single-file motion for ethane, this difference in magnitude is explicable.

If, on the contrary, we postulate that ethane undergoes ordinary motion, then this ratio of MSDs can not be explained. Moreover, there is evidence we can employ to disprove it. This evidence is based upon the density dependence of the diffusivity. For both methane and ethane, we can run simulations at infinite dilution. The infinite dilution diffusivities of methane and ethane (5 Å) at $T = 298°K$ in $AlPO_4$-5 are, respectively, $1.2 \times 10^{-3}\, cm^2/s$ and $7.7 \times 10^{-4}\, cm^2/s$. (At infinite dilution, all fluids are ordinary diffusers since there is no question of passing and no other atoms to form a single file.) The ratio of methane to ethane infinite dilution diffusivities is 1.56. (We expect a higher diffusivity for methane because it has a lighter mass, and in dilute solution, the diffusivity scales as one over the square root of the molecular weight.[19] This would lead to a ratio of 1.37. Methane is also smaller and should be able to move more freely within the nanopore, which explains why we see a ratio greater than 1.37.)

To a first-order approximation, the density dependence of the diffusivity in a dilute fluid is independent of fluid identity and scales as one over the molar density.[19] Therefore, we should expect that the ratio of methane to ethane diffusivities (or MSDs) should remain constant, up to intermediate loadings. The value of that ratio obtained at infinite dilution, 1.56, should be maintained at finite loadings, all other things being equal. However, the ratio of simulated MSDs for methane to ethane is 10.5 (c.f. 1.56 at infinite dilution). Since the only variable that changes is the density and since the density dependence cannot explain the result, there must be another mechanism involved. That mechanism is the single-file motion of ethane.

Since we are conducting molecular-level simulations, we have two additional criteria to confirm single-file motion. The third criterion is that we can number the atoms and record when they pass. Using this technique, it has been and, in this work, is again verified that ethane (both 5 Å and 6 Å) does not pass but that methane does pass. The last criterion is that we can watch movies of the simulation, visually observing any passing. These movies clearly show the different modes of motion. It is obvious from these movies that methane molecules dart about quickly and pass each other. The chain of ethane molecules moves much more slowly along the channel. Movies of pure methane, pure ethane, and methane/ethane mixtures diffusing in $AlPO_4$-5 are available for public viewing on the Internet.[20]

3.2. Demonstration of the Separation Mechanism

What has been shown to date is that ethane undergoes a much slower mode of motion in $AlPO_4$-5 than does methane. In order to effect a kinetic separation, we must exploit this difference in mobility. In short, we must show that methane is able to pass ethane in $AlPO_4$-5 and thus retain its high ordinary diffusivity. We simulated a 50.0 mole percent methane, $x_M = .5$, mixture. The temperature was 298°K and the loading was 1.0 molecules per unit cell $AlPO_4$-5. MSDvT plots are shown in Figs. 5 and 6 for ethane of diameters 5.0 and 6.0 Å, respectively. The resulting diffusivities, single-file mobilities, and measures of fit are shown in Table 2.

The case of methane and 5-Å ethane corresponds to case (c), where methane passes methane, ethane cannot pass ethane, and methane passes ethane. By ordering the molecules (criterion three), we confirm that methane can pass ethane but that ethane itself remains single-file. The shapes of the ethane single-file MSDvT curves show some noise, based on the long time scale of passing events of the methane and ethane. Applying criterion one,

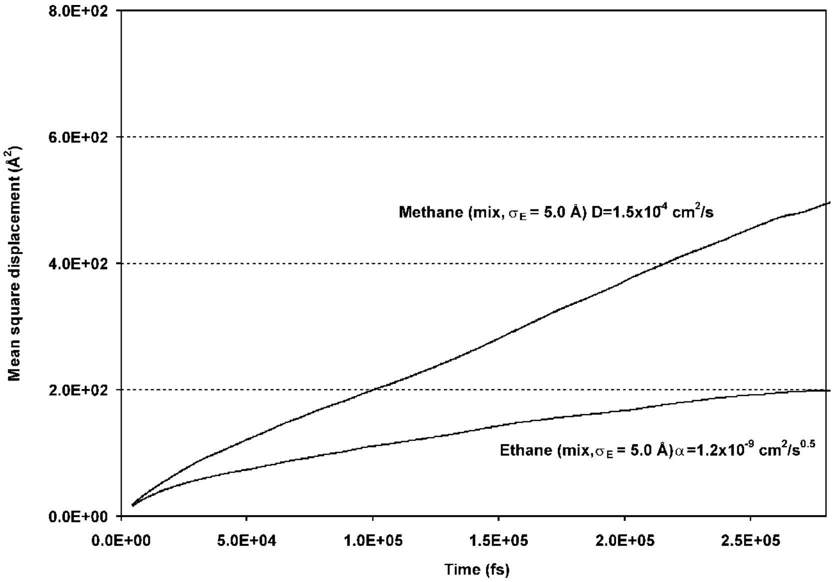

Figure 5. Binary mixture of methane and ethane mean square displacement versus observation time at $T = 298°K$, $\sigma_E = 5.0\,Å$, $\sigma_M = 3.882Å$, $x_M = 0.5$, $N_E + N_M = 1.0$ molecule/unit cell $AlPO_4$-5.

methane better fits Einstein's relation (but not by much) and ethane better fits 1DHR theory.

In Fig. 5, the MSDvT plots show that the methane retains an ordinary diffusivity. In physical terms, this means that methane molecules are able to pass the 5-Å ethane molecules in the pore. Because ethane molecules are larger than methane molecules, they present a larger barrier to pass and thus reduce the diffusivity of the methane from that of a pure methane fluid at the same total density. However, the mean square displacement of the methane remains proportional to the observation time.

Although 5-Å ethane can pass methane, ethane retains a single-file mobility since it cannot pass other ethane. If the methane had absolutely no effect on the mobility of ethane, then we would expect an increase in the mobility of ethane in the mixture over that in the pure component, purely on the basis that the molar density of ethane has decreased (from 1.0 ethane per unit cell in the pure fluid to 0.5 in the mixture), and that affects the single-file mobility as given in Eq. (3). Using Eq. (3) to predict the mobility of ethane at a molar density of 0.5 ethane per unit cell, from that of the pure component

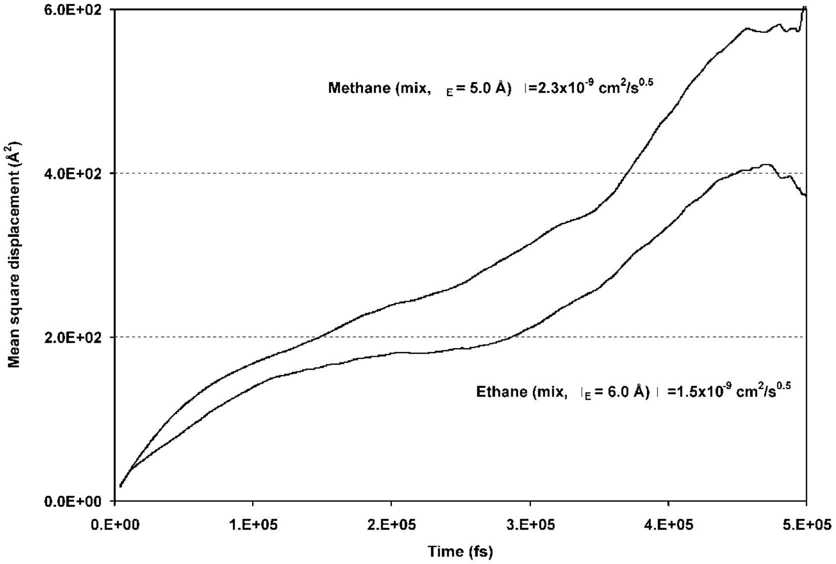

Figure 6. Binary mixture of methane and ethane mean square displacement versus observation time at T = 298°K, $\sigma_E = 6.0\,Å$, $\sigma_M = 3.882\,Å$, $x_M = 0.5$, $N_E + N_M = 1.0$ molecule/unit cell $AlPO_4$-5.

mobility, we find the predicted mobility of ethane in the mixture should increase by a factor of 3.42. Since the observed factor of increase is 1.09, we see that the methane does affect the magnitude of the ethane mobility by an increase in the overall density and thus the number of collisions an ethane molecule experiences.

If we consider criterion two, the magnitudes of the MSDs, we find a ratio of methane MSD to ethane MSD of 4.6 over half a nanosecond. If we scale this to 1 second, using the established time dependence for both fluids, we find a ratio of MSDs of 200,000. In other words, in any separation unit in which the residence time of methane and ethane were one second in $AlPO_4$-5, the simulations predict a factor of 200,000 difference in the ratios of MSDs of methane and ethane.

The case of methane and 6-Å ethane corresponds to case (d), where methane passes methane, ethane cannot pass ethane, and methane cannot pass ethane. By ordering the molecules (criterion three), we confirm that methane passes methane but that it cannot pass ethane. The initial distribution of methane among ethane is retained. Individual members of a cluster of methane, sandwiched between two ethanes, may switch positions within

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the cluster, but no member can leave the cluster. Thus, there is a single-file motion of methane clusters (of various sizes). The shape of the MSD for both methane and ethane is strange. Clearly, it is not linear with either time or the square root of time.

The shape of the curve must be due to events of a time scale that cannot be averaged out in a nanosecond with the system size we are using. These events must be associated with the single-file motion of clusters of random size, randomly distributed among a larger truly single-file component. At this stage, there is no theory to describe the motion or to predict the time scale of computation necessary to capture the true, long-time behavior of this complex system. We should make it clear here that the MSD in Fig. 6 is not indicative of the true long-time MSDvT behavior of a such a system.

However, we can make several important statements about the system depicted in Fig. 6, a case (c) system: The magnitude of the MSDs are roughly equal, and the time behavior of both components is the same. Moreover, since the methane clusters and ethane are single file, in the true long-time behavior, they must eventually have the same single-file mobility factor. (In a single file, they are limited by the slowest member in the file.) Thus, we must conclude that a kinetic separation of this system [a case (c) system] would not be effective.

In Fig. 7, we plot on a semi-log scale the diffusivities and mobilities of methane and ethane (pure and in a 50/50 molar mixture as a function of ethane diameter at $T = 298°K$ and $N_E + N_M = 1.0\,\text{molecules/unit cell}$ $AlPO_4$-5). There is clearly an abrupt transition between ordinary diffusion, with values of diffusivity greater than $10^{-5}\,cm^2/s$, and single-file motion, with values of single-file mobility less than $10^{-8}\,cm^2/s^{0.5}$.

Values with small ethane diameters (4.0 and 4.5 Å) demonstrate case (a) behavior; both pure components exhibit ordinary diffusion, as do their mixture. Intermediate values of the ethane diameter (5.0 and 5.5 Å) display case (d) behavior; one pure species exhibits ordinary diffusion, the other pure species exhibits single-file motion, and in the mixture, the smaller species retains its ordinary diffusive motion. The high value of ethane diameter (6.0 Å) demonstrates case (c) behavior; one pure species exhibits ordinary diffusion, the other pure species exhibits single-file motion, and in the mixture, the smaller species loses its ordinary diffusive motion.

Figure 7 encapsulates the notion that the difference in single-file motion can be exploited to effect a kinetic separation. Of course, in reality, we are not able to adjust the diameter of a molecule to suit our needs. However, hundreds of zeolite and molecular structures exist. Many of these have one-dimensional channels. The one-dimensional channels can be constructed of 12-O-atom rings, as in $AlPO_4$-5. Other structures, however, have 10-O-atom rings

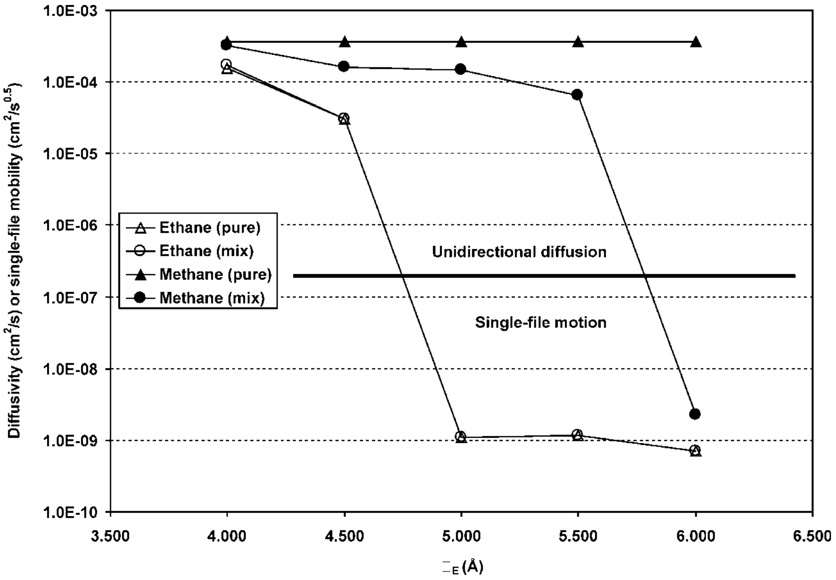

Figure 7. Diffusivities and mobilities of a binary mixture of methane and ethane as a function of ethane size at T = 298°K, $\sigma_M = 3.882\,\text{Å}$, $x_M = 0.5$, $N_E + N_M = 1.0$ molecule/unit cell $AlPO_4$-5.

(zeolite Θ), 14-O-atom rings ($AlPO_4$-8), and 18-O-atom rings (VPI-5). Because the size of the rings that define the channel vary, the size of the channel varies. Moreover, among a given size ring, say the 12-O-atom ring, there are numerous other structures. (In addition to $AlPO_4$-5, there are ZSM-12, zeolite Ω, and zeolite L.) Each of these has a slightly different accessible volume in the channel. Therefore, had it proved that methane could not pass ethane in $AlPO_4$-5, we would have known to look at a larger 12-O-atom channel, like zeolite L. Had it proved that ethane were not single-file in $AlPO_4$-5, we would have known to move to a smaller 12-O-atom channel, like ZSM-12. Foreseeing the need for rough estimates of channel size, Keffer et al. have produced a compendium of potential energy maps that describe the accessible volume of more than 20 zeolites.[1] This tool will allow the intelligent selection of a nanoporous adsorbent for a particular separation need. So, while molecule diameters are not variable, the same intent can be accomplished by selecting the proper zeolite or molecular sieve.

Figure 7 also shows that the pure ethane and ethane in the mixture diffusivities or the mobilities are nearly the same. This demonstrates that the motion of the larger (slower) species is relatively unaffected by the presence of the smaller species, provided the total molar density remains constant. On the other hand, the methane diffusivity is more strongly impacted by the presence of the ethane, provided the ethane is large enough to exhibit single-file motion in the pure fluid. This impact becomes drastic if the ethane is so large that the methane cannot pass it.

3.3. Adsorbate Size Dependence

To fully understand the mechanisms behind the data in Fig. 7 requires a mass transport theory that describes (1) single-file motion of pure components, (2) ordinary diffusion of pure components, (3) motion of mixtures when mixed pairs can't pass [case (c)], and (4) motion of mixtures when mixed pairs can pass. One-dimensional hard-rod theory can describe single-file motion of a pure component. However, a theory that describes the diffusion of a pure component in a unidirectional, energetically heterogeneous, nanoporous environment does not exist. Therefore, we are currently limited in our ability to make predictive models.

However, since we do have one-dimensional hard-rod theory, we can test the size dependence of the single mobility for the pure-component ethane system, using Eq. (3). Equation (3) has an explicit size dependence in σ as well as an implicit size dependence buried in D_{id}. The infinite-dilution diffusivity is also a function of the adsorbate size.

We ran simulations to calculate the infinite dilution diffusivity at each ethane diameter, where ethane was single-file. We then used Eq. (3) to test 1DHR theory to calculate single-file mobilities at finite densities for each ethane diameter. We compared these predictions to simulations conducted at the finite loadings. The results are shown in Fig. 8.

The first thing to note in Fig. 8 is that the infinite dilution diffusivities are nonlinear with increasing ethane diameter. This spread in the data is not due to simulation noise. For each infinite dilution diffusivity, two runs were simulated, one with 128 ethane molecules and one with 256 molecules. In all cases, the independent simulations gave diffusivities within 3% of each other. The average is shown in Fig. 8.

Intuitively, one might expect that the diffusivity decreases as the adsorbate diameter increases, because the collision diameter increased, which shortens the mean free path. However, this is not the case in nanoporous materials. We know in $AlPO_4$-5, potential energy maps and density distributions show us that there are toroid adsorption sites spaced regularly along the channel axis, twice per unit cell. A simple potential energy map (without simulation) of the various sizes of ethane gives an indication of

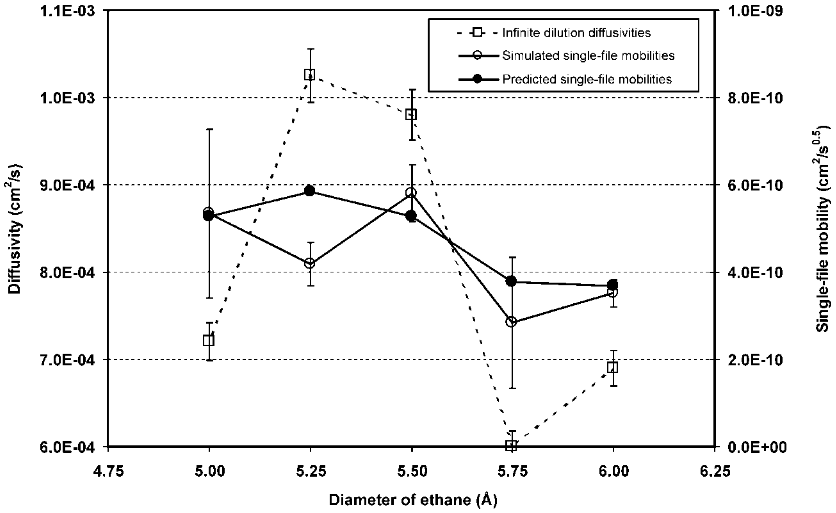

Figure 8. Comparison of one-dimensional hard-rod theory and simulation: dependence on ethane size. $T = 298°K$, $x_E = 1.0$, $N_E = 1.0$ molecule/unit cell $AlPO_4$-5.

whether it is a molecular-level fit, which allows ethane of different diameters to optimize the adsorbate–pore interaction in different ways. Different sizes of molecules may find a particularly favorable niche in an adsorption site (i.e., energy well). Smaller sizes may be too small to optimize the energetics of occupying the niche, and larger sizes may be too large to enter the niche completely. Based purely on activation energies, however, the predicted trend is that the diffusivity increases with increasing adsorbate diameter because the activation energy decreases. It is the entropic term, which incorporates the tight fit of the adsorbate as it passes through the narrow neck in the channel, that opposes the energetic trend and yields a maximum in the diffusivity with respect to adsorbate size.

This nonmonotonic behavior then translates into nonmonotonic behavior for the single-file mobility of ethane at finite loadings.

Comparison of the single-file mobilities, predicted from the infinite-dilution diffusivities and 1DHR theory, with the simulated mobilities does not yield the most compelling agreement. However, the relative error between the predicted and simulated mobilities is less than 32% in all cases. This error is not excessive considering (1) the mobilities are many orders of magnitude smaller than the diffusivities and (2) we are predicting the size dependence of finite-loading mobilities based on infinite-dilution data.

4. CONCLUSIONS

This work has demonstrated unambiguously that the difference in ordinary unidirectional diffusion and single-file motion of adsorbates can be used to effect a kinetic separation in a one-dimensional nanoporous material.

We have shown that, given one component that undergoes ordinary diffusion in the pure fluid and another component that undergoes single-file motion in the pure fluid, a mixture of those two fluids can be separated on a kinetic basis, provided that the molecules of one type can pass molecules of the other type in the nanoporous channel.

Even if single-file motion does not persist over longer times, the difference in the speeds of motion between the component in single-file and the one in ordinary diffusion at short times would contribute to the overall difference in the motion of these two components through the system. This provides a mechanism for a kinetic separation.

We have provided criteria for the experimentalist and the simulations researcher to clearly distinguish between single-file motion and ordinary diffusion, and we have pointed out the strengths and weakness of those criteria. Work is currently in progress developing a predictive theory that describes the temperature, density, and compositional dependence of the motion (both diffusive and single-file) of mixtures in one-dimensional, energetically heterogeneous, nanoporous materials. Work is also planned to test the most serious assumptions in this model, namely using single-body ethane, using a rigid molecular sieve framework, and using a molecular sieve framework devoid of its inherent charge distribution.

NOMENCLATURE

D	diffusivity
D_{id}	infinite dilution diffusivity
ℓ	lattice spacing
MSD	mean square displacement
N_i	one-dimensional number density of species i (molecules/length)
t	time
T	temperature
x_i	mole fraction of component i
α	single-file mobility factor
ε_i	Lennard-Jones energy parameter of species i
σ_i	Lennard-Jones diameter of species i

τ	mean time between successful moves between lattice sites
θ	fractional loading

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We wish to acknowledge the University of Tennessee Computer Science Department for the use of its IBM SP-2 and the University of Tennessee Department of Chemical Engineering for startup funding for this research.

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