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Characterizing adsorbate passage in molecular sieve pores

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Abstract

The rate at which molecules can pass one another inside the pores of crystalline microporous materials can be an important factor in determining the transport properties of these systems, particularly for materials with unidimensional pores. An efficient method for characterizing adsorbate passage in micropores is presented and applied to a variety of adsorbates in $AlPO_4$-5. It is shown that adsorbate passage can be an activated process in some cases. The implications of rare adsorbate passage for the experimental characterization of tracer diffusion and for the flow of multicomponent mixtures through zeolitic membranes are briefly considered in the context of a simplified lattice gas model. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Adsorbate passage; Molecular sieve pores; Tracer diffusion

1. Introduction

The ordered nanometer-scale pores that permeate zeolites and other crystalline microporous materials render these materials ideal for a wide range of applications involving selective sorption and shape-selective catalysis. Many materials exist with unidimensional pores, that is, pores that do not intersect other pores to form a three-dimensional network [1]. One possible difficulty that can be encountered in applications involving sorption in unidimensional pores is that these pores can be subject to transport limitations that do not occur in materials with interconnected pores. In particular, if molecules adsorbed in a unidimensional pore cannot pass one another, they will perform "single-file" diffusion [2–5]. Species that can pass each other inside a pore are said to undergo "normal" diffusion. One of the best known distinctions between species performing single-file and normal diffusion is that rate at which a particular molecule explores the pore as a function of time [2–5].

When adsorbates are large compared to a pore's width, the appearance of single-file diffusion can be unambigously identified. One well-characterized example is the diffusion of CF_4 in $AlPO_4$-5 [3,5]. A more interesting situation arises when adsorbates are roughly half the width of a pore. To date, the unambiguous experimental characterization of diffusion of adsorbates satisfying this criterion has proved difficult. For example, the results of a number of experiments intended to classify the tracer diffusion of small alkanes in the molecular sieve $AlPO_4$-5 [3,6–9] are summarized in Table 1. These results are contradictory, since a species can perform single-file or normal diffusion, but not both. The most plausible interpretation of the discrepancies between these studies is that alkane molecules in $AlPO_4$-5 pores can pass one another, but do so very rarely [7]. In this case, the characteristics of normal diffusion only become evident on long timescales, so experiments that do not probe sufficiently long times can incorrectly identify single-file diffusion. Unfortunately, this hypothesis is difficult to test directly, since no experimental methods are currently available to characterize the passage rates of adsorbed molecules. This observation suggests that it would be useful to be able to accurately describe the characteristics of adsorbate passage in micropores, particularly in systems where the passing of adsorbates is slow compared to other typical timescales for molecular transport.

The use of direct atomic-scale simulations of adsorbed molecules has been an extremely useful complement to experimental studies of molecular transport in unidimensional pores. Molecular dynamics simulations have been used to verify the characteristics of single-file diffusion that are analyzed in experimental data, as well as providing explicit examples of the difficulties of analyzing experimental data when adsorbate passage is possible but rare [4]. Simulations have also been used to classify the types of tracer diffusion that can occur in multi-component mixtures adsorbed in unidimensional pores [5] and to show that collective motions of loosely bound clusters of adsorbates

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Table 1
Experimental determinations of the diffusion mode of alkanes adsorbed in $AlPO_4$-5 using pulsed field gradient nuclear magnetic resonance (PFG-NMR), quasi-elastic neutron scattering (QENS), or zero length chromatography (ZLC)

Adsorbate	Reference	Method	Reported mode
CH_4	3	PFG-NMR	Single-file
	6	PFG-NMR	Normal
	7	QENS	Normal
C_2H_6	8	PFG-NMR	Single-file
	7	QENS	Normal
C_3H_8	9	ZLC	Normal

can make important contributions to molecular transport in some single-file systems [10]. Despite these successes, no simulations have been performed that can clearly characterize if and how molecules can pass one another in a micropore. The principal technique that has been used to address this issue has been large-scale molecular dynamics (MD) simulations. By examining the ordering of molecules in a pore as a function of time, it is straightforward to determine if molecules can pass one another [4,5]. Unfortunately, the computational expense associated with simulating a large number of passage events is prohibitive when the rate of molecular passing is slow.

The aim of this paper is to introduce a technique that allows adsorbate passage in micropores to be characterized directly and efficiently. This technique involves computing the free energy of an isolated pair of adsorbed molecules as a function of their relative position. The technique is described in Section 2, and illustrated for two simple models. In Section 3, the behavior of several adsorbed species in $AlPO_4$-5 is discussed. Some of the implications of our findings for experimental studies are briefly discussed in Section 4.

2. Free energy of adsorbate passage

In this section, a technique for directly characterizing the passage of adsorbed molecules in micropores is introduced and illustrated with several simple examples. We assume that an atomic-scale model of the pore and adsorbed molecules is available that defines the potential energy, U, of the total system as a function of the relevant coordinates (adsorbate positions, adsorbate conformations, framework atom positions, etc.) and the the pores are aligned along the z axis. We consider a pair of adsorbed molecules, whose center of masses lie at $z=z_1$ and z_2. The difference in Helmholtz free energy between pairs of molecules with center of mass coordinates z and z' can be calculated using a standard result from Statistical Perturbation Theory [11–13]:

$$A(z') - A(z) = -k_B T \ln\langle e^{-[U(z')-U(z)]/k_B T}\rangle_z. \quad (1)$$

In this expression, $\langle\ldots\rangle_z$ represents a canonical average over the distribution of configurations of the system defined by the coordinate z [11–13]. For the specific problem described above, this average is calculated by constraining the z coordinates of the two molecules to be $z=(z_1, z_2)$ and computing a canonical average over all the other coordinates of the system. These coordinates include the center of mass coordinates transverse to the pore direction, namely x_1, x_2, y_1 and y_2, the orientation and conformation of the molecules if the molecules have internal degrees of freedom, and the coordinates of the framework atoms making up the micropore if a flexible lattice is used. Eq. (1) is formally exact, but in practise the average must be computed numerically using Monte-Carlo methods [11–13].

The first example we will examine is two spheres of radius r inside a cylindrical pore of radius R with hard wall potentials for both the adsorbate–adsorbate and adsorbate–pore interactions. In this case, the average in Eq. (1) is equal to the ratio of the free volumes at each of the coordinates. It is natural to define $A(z)=0$ for $|z_2-z_1|>2r$. The free energy profiles for spheres of several different radii are shown in Fig. 1 as a function of the distance d between the spheres. The free energy required for the spheres to pass one another increases as the size of the spheres is increased. Direct examination of Eq. (1) shows that the free energy profile diverges for $r/R\geq 1/2$. That is, pairs of spheres with $r/R\geq 1/2$ cannot pass one another, while smaller spheres can pass one another by surmounting a finite free energy barrier. This result is the basis of the simplest geometric criterion for distinguishing between systems displaying single-file and normal diffusion [3–5]. It will be shown below, and has been observed in MD simulations [4,5], that the behavior of more realistic models is more subtle. It is noteworthy that the free energy barriers that appear in this model are entirely due to entropic effects.

As a second example, we modify the model above by retaining the hard-wall adsorbate–pore interactions but change the adsorbate–adsorbate interaction to a Lennard-

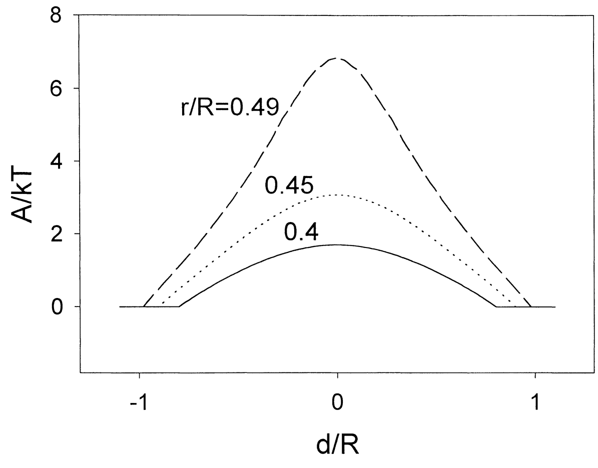

Fig. 1. Free energy profiles for pairs of hard spheres in a hard walled cylinder for three values of r/R.

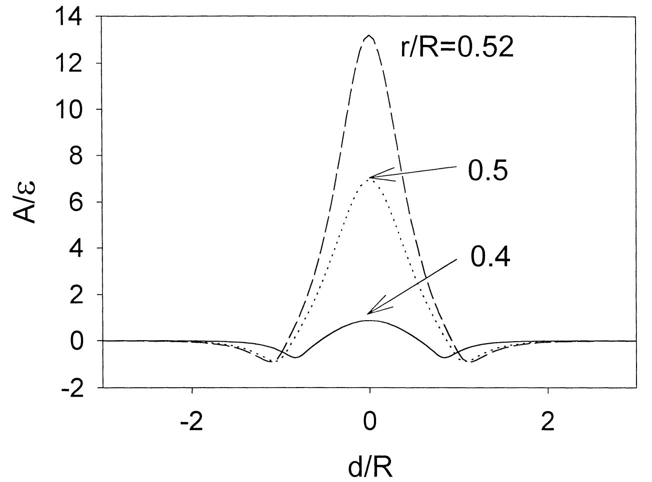

Fig. 2. Free energy profiles for pairs of Lennard-Jones spheres in a hard walled cylinder for three values of r/R with $\varepsilon/k_BT=1$.

Jones potential with $\sigma=2r$ and binding energy ϵ. The free energy profiles for the model for several values of r/R are shown in Fig. 2. Two qualitative differences between the hard-sphere and Lennard-Jones sphere results can be observed from Figs. 1 and 2. First, free energy minima appear in the Lennard-Jones system when the adsorbates are close to one another, due to the attractive energy between the particles. Secondly, the free energy barrier to adsorbate passage does not diverge for $r/R\geq 1/2$ for the Lennard-Jones model, although the barrier does increase rapidly as r/R is increased. This observation would also apply to any other model potential in which the repulsive core of the adsorbate–adsorbate potential is a continuous function. As a result, it is not possible to make a definitive distinction between systems that will perform normal and single-file diffusion in models with continuous potentials.

The free energy barrier to adsorbate passage, $\Delta A_{\mathrm{passage}}$, in the model just discussed is a combination of energetic and entropic contributions. With $\Delta A_{\mathrm{passage}}$ defined to be the difference between the free energy maxima and minima, it is useful to write the free energy barrier as

$$\Delta A_{\mathrm{passage}} = \Delta U_{\mathrm{passage}} - T\Delta S_{\mathrm{passage}}, \qquad (2)$$

and assume that $\Delta U_{\mathrm{passage}}$ and $\Delta S_{\mathrm{passage}}$ are constants. The energetic and entropic contributions can then be extracted by computing $\Delta A_{\mathrm{passage}}$ over a range of temperatures. Performing this calculation for the Lennard-Jones model described above shows that $\Delta S_{\mathrm{passage}}$ is negative for all r and decreases monotonically with increasing r. The behavior of $\Delta U_{\mathrm{passage}}$ is more interesting. For r/R less than approximately 0.48, $\Delta U_{\mathrm{passage}}$ is zero. But as r/R is increased beyond 0.48, $\Delta U_{\mathrm{passage}}$ becomes positive and grows rapidly. That is, for $r/R>0.48$, adsorbate passage in this model is an activated process, with a highly size dependent activation energy. The appearence of an activation barrier to adsorbate passage in this extremely simple model indicates that these barriers will be generic features of all systems in which adsorbate passage involves the adsorbates approaching each other very closely. The existence of activation barriers for adsorbate passage has been inferred experimentally by Karger and Ruthven in studies of propane diffusion in $AlPO_4$-5 [9]. These observations suggest that it may be useful to separate adsorbates into those which exhibit only an entropic barrier to passage (i.e., $\Delta U_{\mathrm{passage}}=0$) and those for which passage is an activated event. In systems where $\Delta U_{\mathrm{passage}}=0$, molecular transport will clearly occur by normal diffusion. If $\Delta U_{\mathrm{passage}}/k_BT=\mathcal{O}(1)$, adsorbate passage will occur, although the passage rate may be slow compared to the hopping rate of isolated molecules. On the other hand, if $\Delta U_{\mathrm{passage}}/k_BT\gg 1$, the passage rate will be negligibly slow and it is reasonable to conclude that molecular transport occurs by single-file diffusion.

3. Adsorbates in $AlPO_4$-5

In this section, the methods discussed above are applied to a detailed model of the molecular sieve $AlPO_4$-5. This material has unidimensional pores with nominal diameter 7.3 Å [1] and has been the focus of numerous experimental and theoretical studies [3–10]. The methods used here for modeling the adsorbate-pore interactions have been described in detail elsewhere [4,5]. Briefly, the atomic coordinates of the pore are taken from experimental crystallographic data and the pore is assumed to be rigid. The adsorbate–pore interaction is taken to be a pairwise sum of Lennard-Jones interactions between the adsorbate and the O atoms in the pore framework. Lennard-Jones interactions are also used to define the adsorbate–adsorbate interactions. The motion of an isolated adsorbate along the pore is an activated process with an activation energy determined by the size of the adsorbate and the strength of the adsorbate–pore interaction [5].

In the simple models discussed in the previous section, the free energy of a pair of adsorbates was only a function of the distance between the molecules, $A(z_1,z_2)=A(|z_1-z_2|)$. For any atomically detailed model of a pore, the inherent structure of the pore means that the adsorbate coordinates must be considered independently and the free energy surface as a function of z_1 and z_2 must be computed. To compute this surface, the region of interest was discretized into a two-dimensional grid. First, the free energy profiles along a series of lines across the grid were computed using Eq. (1). Finally, the free energy profile for the line defined by the starting points of the lines described above was computed. This final profile defines the free energy differences between points on separate lines in the first set of profiles and therefore allows the free energy profile to be defined on the entire grid. The speed of these calculations was substantially enhanced by using double windowing along each integration path [11] and by accelerating the Metropolis sampling of the Monte-Carlo simulations using Umbrella Sampling [14,15]. For each of the adsorbates

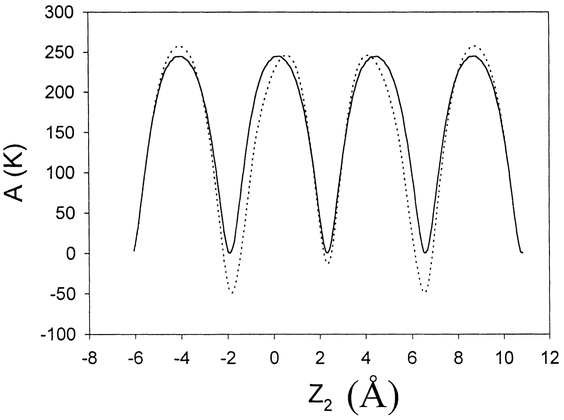

Fig. 3. Minimum free energy paths for motion of a single Ar atom (solid curve) and for Ar passage (dotted curve) in AlPO$_4$-5 at $T=100$ K.

discussed below, the computed free energy surface was analyzed to determine the minimum free energy path (MFEP) for adsorbate passage by determining a parabolic path between adjacent free energy minima that minimized the free energy barrier between the minima. The path obtained in this way provides an excellent approximation to the true MFEP and is exact at the free energy minima and saddle points.

Two examples of minimum energy paths for adsorbate passage are shown in Figs. 3 and 4 for Ar and Xe adsorbed in AlPO$_4$-5. The Lennard-Jones radii of the adsorbate–adsorbate interactions was 3.418 Å (4.055 Å) and the radii for the adsorbate–pore interactions was 3.329 Å (3.547Å) for Ar (Xe). Recall that the nominal diameter of the AlPO$_4$-5 pore is 7.3 Å. In each case, the MFEP for an isolated monomer is shown by the solid curve and the MFEP for one adsorbate moving past another is shown as a dotted curve. For the Ar dimer, the other adsorbate of the pair stays practically fixed at the monomer free energy minimum ($z_1 \simeq 2$ Å) during the adsorbate passage MFEP. This adsorbate also stays close to $z_1 \simeq 2$ Å during the Xe dimer's MFEP, although the free energy maximum in the dimer profile is lowered by allowing this adsorbate to shift slightly along the pore away from the moving adsorbate. The profile shown in Fig. 4 is this optimized path. The MFEPs for adsorbate passage of Ar and Xe are dramatically different. For Ar, there are only minor differences between the monomer and dimer MFEPs, indicating that Ar molecules can pass one another freely in AlPO$_4$-5. For Xe, the free energy barrier to adsorbate passage is much greater than the barrier for an isolated monomer to diffuse. Evaluating the activation energy for passage as described in Section 2 yields, $\Delta U^{\mathrm{Xe}}_{\mathrm{passage}}=910$ K. For comparison, the actvation energy for diffusion of an isolated Xe molecule is 327 K [5]. These results are in excellent agreement with large-scale MD simulations of these systems, which indicated that Ar molecules can pass one another freely but the passage of two Xe molecules is a rare event [5].

The character of the adsorbate passage MFEP can change rapidly as a function of adsorbate size. To illustrate this point, the MFEP profiles for adsorbate passage of methane in AlPO$_4$-5 are shown in Fig. 5 using two different intermolecular potentials that have been developed for this system [4,5]. In both cases, methane is represented by a single united atom. The same methane–methane potential

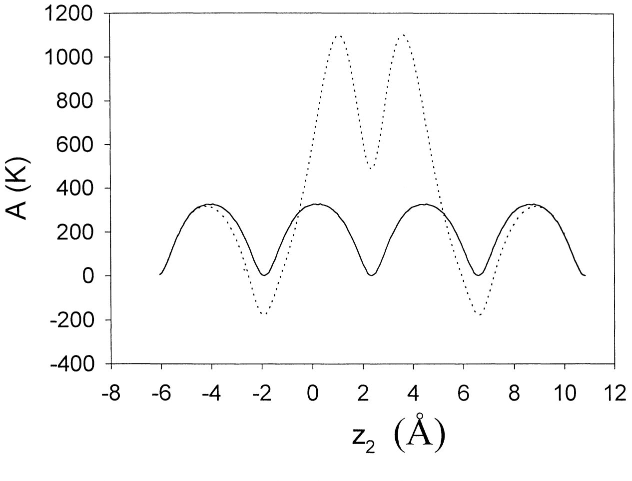

Fig. 4. The same as for Fig. 3 but for absorbed Xe.

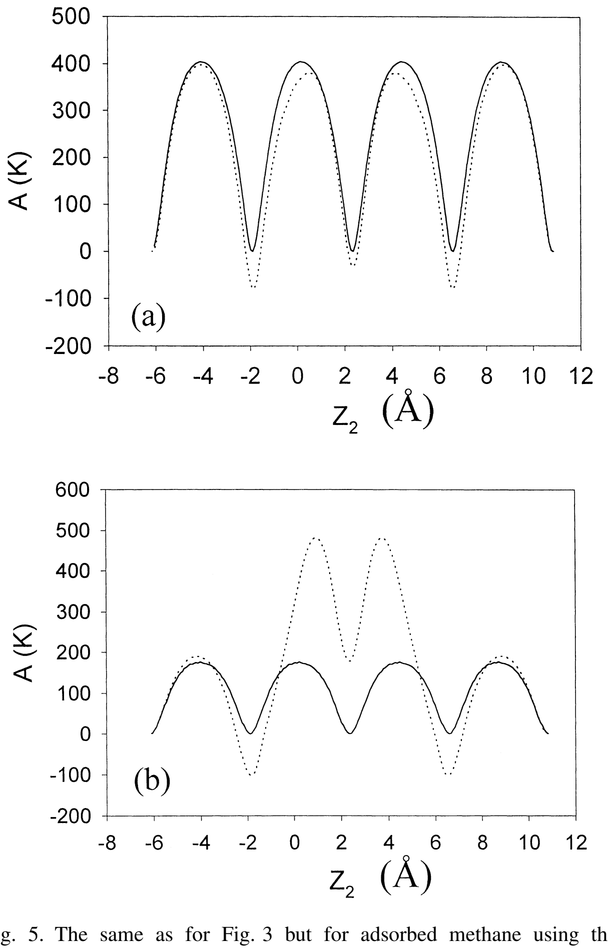

Fig. 5. The same as for Fig. 3 but for adsorbed methane using the intermolecular potential of (a) [4] and (b) [5].

was used in both calculations [4,5]. For the data shown in Fig. 5(a) [(b)], the methane–O interaction was a Lennard-Jones potential with $\varepsilon=141$ [70.5] K and $\sigma=3.08$ [3.46] Å. The potential with the smaller σ yields results quite similar to Ar (cf. Fig. 3): the MFEPs for a monomer diffusing along the pore and for adsorbate passage are quite similar. The potential with the larger σ, on the other hand, yields results very similar to those discussed above for Xe: the passage of two adsorbates requires that a free energy barrier much larger than the barrier for monomer diffusion be surmounted. This observation is consistent with the characterization of methane diffusion as single-file with experiments probing short timescales but normal diffusion in experiments probing longer times [7].

The examples discussed above were all adsorbates which can easily be represented by a single spherical particle. When the diffusion of molecules with more complex shapes in unidimensional pores is considered, it is important that the molecule's shape be accurately described. Eq. (1) offers a straightforward way to accomplish this task. This capability is illustrated in Fig. 6, which compares the MFEP for adsorbate passage in $AlPO_4$-5 for a pair of methane molecules and a pair of ethane molecules. Each ethane molecule was modeled by two Lennard-Jones spheres separated by a rigid bond of length 1.53 Å. The methane potential of [5] were used for the interactions between united atoms in different molecules and the interactions between united atoms and the pore framework. To apply Eq. (1) to ethane, the center of mass of each molecule was constrained while averaging over all orientations of each molecule. The MFEPs for adsorbate passage are qualitatively similar from methane and ethane, with both species exhibiting a large barrier to passage relative to the monomer diffusion barrier. Both the free energy barriers for adsorbate passage and monomer diffusion are larger for ethane than for methane.

The analysis above shows how examining the free energy of a pair of adsorbates can give a useful qualitative characterization of adsorbate passage. When adsorbate passage is an activated process, it is also useful to quantitatively determine the rates of various processes of interest. To demonstrate this process, we return to the passage of Xe molecules in $AlPO_4$-5. An estimate of the relevant timescales is given by assuming that the rate of each activated process is $k=\upsilon \exp(-\Delta U/k_BT)$, where ΔU is the activation energy and υ is a process-independent preexponential factor. For an isolated Xe atom, the activation energy for diffusion is $\Delta U_0=327$ K, so the typical timescale for monomer diffusion is $\tau_0=\exp(\Delta U_0/k_BT)/\upsilon$. For two Xe atoms initially located in adjacent binding sites in the pore, two activated processes with $\Delta U_1=910$ K and $\Delta U_2=584$ K must take place for adsorbate passage to occur (cf. Fig. 4). Defining the typical timescale for these processes to occur to be τ_{passage}, we have

$$\frac{\tau_{\text{passage}}}{\tau_0}=\frac{e^{+\Delta U_1/k_{\mathrm{BT}}}+e^{+\Delta U_2/k_{\mathrm{BT}}}}{e^{+\Delta U_0/k_{\mathrm{BT}}}}. \quad (3)$$

This ratio increases from 9.4 at 300 K to 353 at 100 K. It is important to note that the timescales just discussed are not sufficient to determine the total rate of adsorbate passage events in a pore, since this rate is influenced not only by τ_{passage} but also by the density of pairs of Xe atoms in the pore. Moreover, other activated processes can also contribute to the adsorbate passage rate. For example, the activation energies for a Xe atom to move past two other Xe atoms located in adjacent sites are not the same as the activation energies for the processes discussed above. These observations suggest that an accurate model for the diffusion of Xe in $AlPO_4$-5 may be derived by cataloging the various processes that allow Xe atoms to hop between binding sites [16] and using the free energy profiles of these processes to derive their activation energies. Once this information is available, a lattice gas model for the system can be constructed that will allow simulations of Xe diffusion to be performed orders of magnitude faster than with direct MD simulations [16,17]. Work on this topic is currently in progress.

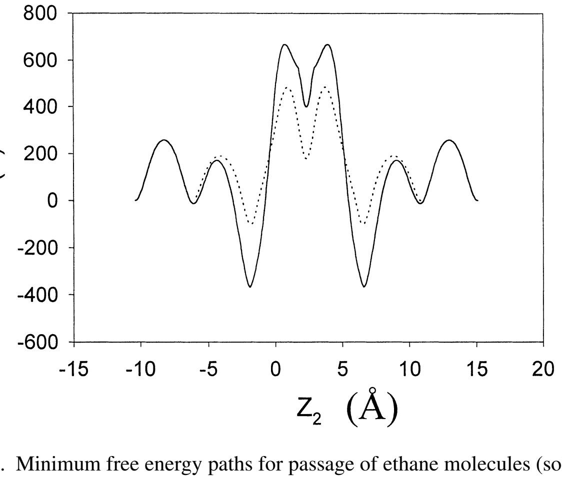

Fig. 6. Minimum free energy paths for passage of ethane molecules (solid curve) and methane molecules (dotted curve) in $AlPO_4$-5 at $T=100$ K.

4. Implications of rare adsorbate passage

It was argued above that when both the diffusion of isolated molecules and the passing of molecules in a pore are activated processes, molecular transport can be effectively modeled by deriving a lattice gas (LG) model. In this section, a very simple LG model of adsorbate diffusion in unidimensional pores is considered to briefly illustrate some of the implications of rare adsorbate passage in experimentally relevant situations. This model is based on a model presented by Qureshi and Wei [18]. The unidimensional pore is represented by a one-dimensional array of sites, and it is assumed that at the most one adsorbate may occupy a given site. The probability that a site is occupied is denoted by θ. Particles of species i are assumed to hop into neighboring empty sites at rate k_i. To include the effects of adsorbate passage, particles of species *i* and *j* are allowed to exchange positions on the lattice at rate k_{ij} when they occupy neighboring sites. Although it is clear from the results above that detailed LG models of activated transport in unidimensional pores must usually include multiple classes of moves leading to adsorbate passage [19], this simple model is useful because it gives an indication of the types of questions that can be addressed once more detailed models are derived.

4.1. Characterizing tracer diffusion

We first consider a pore containing only one species at a specified loading, θ, and ask: if we can measure the mean-square displacement of individual particles in the pore, can we classify the diffusion as normal or single-file? Experimental resolution of this question typically relies on the observation that at long time, the mean squre displacement of a tagged particle, $\langle z^2(t)\rangle$, obeys

$$\langle z^2(t)\rangle \propto t^{\alpha}, \tag{4}$$

with α=1 (1/2) for normal (single-file) diffusion. When adsorbate passage occurs but is rare, the time dependence of $\langle z^2(t)\rangle$ is more complex [4]. One way to quantify this effect is to allow the scaling exponent, α, to be time-dependent by defining

$$\alpha(t) = \frac{\partial \ln\langle z^2(t)\rangle}{\partial \ln t}. \tag{5}$$

The values of $\alpha(t)$ for the LG model defined above with θ=0.2 and various values of f=k_{11}/k_1 are shown in Fig. 7. This data was generated from kinetic Monte-Carlo simulations of the LG model [20]. Simulations with other values of θ yield qualitatively similar results.

Fig. 7 shows that $\alpha(t)$ takes values between 0 and 1 for observation times that are large compared to the time necessary for an isolated particle to hop, particularly when $f \ll 1$. For all f>0, $\alpha \rightarrow 1$ as $t \rightarrow \infty$, but as the data in Fig. 7 demonstrates, the time required to actually observe this limiting value can be very large. Similar results have been observed in MD simulations [4]. These results all point out that if information about the mode of adsorbate diffusion is to be determined from $\langle z^2(t)\rangle$, it is vital that data be recorded over the longest practical range of time. Since activation barriers for adsorbate passage will be common in systems where passage is rare, the difficulties associated with analyzing the mean square displacement can be reduced by increasing the temperature at which the data is taken.

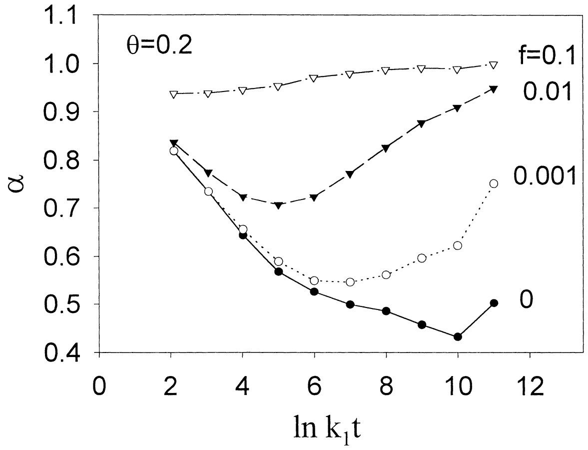

Fig. 7. Effective scaling exponents for the lattice gas model described in the text.

4.2. Multi-component transport through membranes

We now turn our attention to the transport of multi-component adsorbate mixtures through microporous membranes. Considerable progress has been made in recent years towards the reliable synthesis of oriented zeolitic membranes, and experimental studies have demonstrated the exciting possiblities these membranes will allow [21–25]. Microporous materials with unidimensional pore structures offer a conceptually simple way to make membranes, since each pore acts independently of the others. To examine a simple model of a single pore membrane, we consider a pore that extends from x=0 to x=L. Since typical membrane thicknesses are 1–10 µm [21–25], compared to typical unit cell sizes of 5–10 Å in unidimensional pores [1], it is useful to consider a continuum limit of the LG model defined above [18]. In this limit, the occupancy of the pore by species *i* at position *x* is denoted by $\theta_i(x)$. By making a mean-field assumption [18], the time-dependence of the concentration profiles may be written in closed form as

$$\frac{\partial \theta_i}{\partial t} = k_i a^2 \nabla^2 \theta_i + \sum_{i \neq j} a^2 (k_{ij} - k_i)(\theta_j \nabla^2 \theta_i - \theta_i \nabla^2 \theta_j). \tag{6}$$

In this expression, ∇^2=$\partial^2/\partial x^2$ and a is the lattice constant. For convenience, all results below are presented in units where a=1. If k_{ij}=0, this expression reduces to Qureshi and Wei's result [18]. Eq. (6) is independent of k_{ii}, so the possibility of molecules of the same species passing one another has no effect on the macroscopic response of membranes to single-component feeds in this model. The steady-state solution of Eq. (6) is

$$\theta_i(x) = \theta_i^0 + \frac{x}{L}\,\delta\theta_i, \tag{7}$$

where $\delta\theta_i = \theta_i^L - \theta_i^0$ and $\theta_i^0(\theta_i^L)$ is the loading at x=0(L). The loadings at the pore boundaries are usually assumed to be given by the equilibrium adsorption isotherms for the known external pressures [18], although deviations from these values occur if mass transfer resistances at the pore boundaries cannot be neglected [26]. The flux of species *i* is given by

$$J_i = -k_i \nabla \theta_i + \sum_{i \neq j} (k_i - k_{ij})(\theta_j \nabla \theta_i - \theta_i \nabla \theta_j). \tag{8}$$

Once the loadings at the pore boundaries are known, the steady-state fluxes, J_i, are given by

$$LJ_i = -k_i\,\delta\theta_i + \sum_{i\neq j}(k_i - k_{ij})(\theta_j^0\,\delta\theta_i - \theta_i^0\,\delta\theta_j). \qquad (9)$$

We now consider a two-component adsorbate mixture. One way to use a microporous membrane is to allow a gas phase mixture to contact one end of the membrane while minimizing the total downstream pressure to maximize the total permeability. This situation can be modeled by setting $\theta_1^L = \theta_2^L = 0$, which gives the steady-state fluxes as $J_i = k_i\theta_i^0/L$ (i=1,2). Thus, in this situation the steady-state flux is independent of the adsorbate passage rate. A somewhat different scenario that is often realized in experimental measurements of membrane permeability is to allow one species to adsorb into one side of the membrane while equalizing the pressure on the other side of the membrane with a sweep gas [22–25]. In general, some counterdiffusion of the sweep gas across the membrane is expected. Setting $\theta_2^0 = \theta_1^L = 0$ and letting θ_1^0 and θ_2^L be non-zero, the steady state fluxes are

$$LJ_1 = k_1\theta_1^0(1-\theta_2^L) + k_{12}\theta_1^0\theta_2^L. \qquad (10)$$

$$LJ_2 = k_2\theta_2^L(\theta_1^0 - 1) - k_{12}\theta_1^0\theta_2^L, \qquad (11)$$

Note that $J_2<0$ and $J_1>0$, so in both cases the possibility of adsorbate passage increases the steady-state flux. One interesting limit of this scenario is when the loading of the sweep gas at the downstream boundary is high, that is, when $\theta_2^L \simeq 1$. In this case, the flux of species 1 across the membrane is $J_1 \simeq k_{12}\theta_1^0/L$. That is, in this case the flux of species 1 is determined almost entirely by the adsorbate exchange rate (k_{12}), not by its own hopping rate (k_1). This is an example of a situation where the Fickian diffusion coefficient of the permeating species of interest (species 1) has little bearing on the actual steady-state flux through a membrane.

5. Conclusion

Determining if adsorbates can pass one another during diffusion in a micropore is an important step in characterizing molecular transport in unidimensional pores. Atomically detailed simulations are an ideal avenue for studying this issue, which is challenging to examine experimentally. Although Molecular Dynamics can be used to examine the passage of adsorbates, these simulations are very inefficient when adsorbate passage is rare. In this paper, an alternative technique for characterizing adsorbate passage has been introduced. This technique uses Monte-Carlo simulations to compute the free energy of a pair of adsorbates as a function of their positions in a pore. By repeating this calculation at a variety of temperatures, the energetic and entropic contributions to free energy barriers can be extracted. Applying this technique to a series of adsorbates in $AlPO_4$-5 pores demonstrated that for adsorbates of an appropriate size, the passing of two molecules in a pore is an activated process. The existence of activation barriers for adsorbate passage should be a general feature of any physical system in which adsorbates must approach each other closely in order to pass in a pore. Analysis of adsorbate free energies provides a direct method for quantifying the activation energies of multi-adsorbate events and should prove useful in the derivation of coarse-grained models of adsorbate dynamics.

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