The importance of boundary effects in diffusion of hydrocarbon molecules in a one-dimensional zeolite channel

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Abstract. Single-file diffusion of propane and toluene molecules inside a narrow, effectively one-dimensional zeolite pore was experimentally studied by Czaplewski et al. Using a stochastic lattice gas approach, we obtain an analytical description of this process for the case of single-component loading. We show that a good quantitative agreement with the experimental data for the desorption temperature of the hydrocarbon molecules can be obtained if the process of desorption from the boundary is associated with a higher activation energy than the diffusion process in the bulk. We also present dynamical Monte Carlo simulation results for two-component loading which demonstrate in agreement with the experimental findings the effects of mutual blockage of the molecules due to single-file diffusion.

Keywords: driven diffusive systems (theory), stochastic particle dynamics (theory), stochastic processes (theory), diffusion
1. Introduction

Zeolites are microporous crystalline materials which have wide industrial applications. Because of their regular pore structure of molecular dimension, zeolites are often used as ‘molecular sieves’ to selectively sort molecules on the basis of their size (or shape). In a wide variety of chemical and petrochemical processes, zeolite channels are used as catalysts and adsorbents of hydrocarbon molecules. It is important to understand the mechanism of transport of molecules within a zeolite channel and their exchange with the surrounding gas phase in order to design more efficient use of such materials.

In this paper we describe a lattice gas model for explaining the mechanism of transport and desorption of hydrocarbon molecules in a quasi-one-dimensional zeolite channel. In particular, we aim to explain quantitatively the experimental observation of single-file diffusion by Czaplewski et al [1]. An earlier study shows that, using activated diffusion of hard-core particles on a one-dimensional lattice, one can explain the important features of the experimental data qualitatively [2]. However, no quantitative comparison was possible within that simple model. In this paper we address the question: which physical mechanism is responsible for this failure? We find that boundary effects in the form of a higher activation energy for desorption of molecules play a crucial role. With judiciously chosen desorption barriers we can match our analytical and numerical results quantitatively with the experimental data. In the remaining part of the introduction, we present the main idea of the experiment in [1] and we briefly illustrate our modeling strategy.

In [1] Czaplewski et al have demonstrated in an experiment that it is possible to trap the light hydrocarbon (propane) molecules in the presence of the heavier ones (toluene) inside a narrow zeolite channel. Toluene molecules are strongly adsorbed in the zeolite and consequently need a high temperature in order to desorb from the channel, whereas the propane molecules, being weakly adsorbed, have a rather low desorption temperature. If a mixture of toluene and propane is present inside a narrow channel of the zeolite of type EUO, then, because of the confining pore dimension, the molecules cannot pass...
each other (see figure 1). In such an effectively one-dimensional motion of the molecules the more strongly adsorbed toluene molecules block the movement of the less strongly adsorbed propane molecules. As a result, propane is not able to desorb until toluene has desorbed, which occurs at a high temperature. Thus the effective desorption temperature of propane is raised in the presence of toluene.

We aim to describe the main features of the above experimental observation using a stochastic lattice gas approach. Following Kärg er et al. [3, 4], we model the narrow pore of the zeolite using a one-dimensional lattice and the hydrocarbon molecules as a set of hard-core particles diffusing on that lattice. As shown in [2], this simple picture can indeed be used to explain the main experimental results qualitatively. Using an Arrhenius form for activated diffusion of the hard-core particles on the lattice, we have been able to show that the presence of strongly adsorbed particles raises the desorption temperature of the weakly adsorbed ones, in conformity with the experimental observation in [1]. However, this approach predicts a desorption temperature which is much higher than the experimentally observed value.

In order to achieve progress, we suggest that the evaporation of molecules at the boundary of the lattice is associated with a larger activation energy than the diffusion at the bulk. In a real system, the presence of such a desorption barrier near the exit of the channel to the gas phase can be explained by considering the attractive van der Waals interaction between the molecules and the pore wall. When a molecule leaves the pore of a zeolite, it loses its close proximity with the lattice atoms and moves out into a low pressure gas phase, thereby giving up favorable dispersion energy [5, 6].

In section 2 we give a brief description of the experiment [1] and of our previous work on modeling the experimental setting [2, 7]. In section 3 we consider the presence of the desorption barrier. We present an analytical approach for studying single-component loading to demonstrate how the single-component desorption profile changes after incorporating the desorption barrier. In section 4 we present our dynamical Monte Carlo simulation results for the two-component system.

2. One-dimensional zeolites as hydrocarbon traps: experiment and modeling

For the sake of the self-containedness of this paper, we describe in this section the experiment carried out by Czaplews ki et al. to demonstrate the use of narrow zeolite channels as hydrocarbon traps. In the second half of this section we summarize our
Figure 2. Experimental data for the desorption profile as a function of temperature for propane and toluene in a binary mixture in the zeolite EUO, as measured by Czaplewski et al. Data points are taken from figure 5 of [1].

earlier results obtained from the lattice gas approach that we develop further in the bulk of the paper.

2.1. An outline of the experiment of Czaplewski et al

Several different zeolite samples with one-dimensional channels or with three-dimensional pore-network connectivity were considered. The zeolite samples were loaded with an equimolar binary mixture of propane and toluene and, for reference purposes, also with single-component propane and toluene separately. After the loading was complete, the whole system was purged in pure helium such that no hydrocarbon molecules remain outside the channels. Then the system was heated at a constant rate and the flow of the hydrocarbon molecules out of the channel was monitored as a function of temperature. This is known as ‘temperature programmed desorption’ (TPD).

For the single-component loading, it was found that the current initially grows with temperature, shows a peak and then falls off to zero. The desorption temperature of each component was measured at the position of the peak. For the purpose of our modeling we will be interested in the TPD profile of the EUO zeolite (see [2] for details). When only propane was loaded into the one-dimensional channel of EUO, the desorption peak was found at the temperature 40 °C. For single-component toluene the desorption temperature was 80 °C, toluene being more strongly adsorbed. For an equimolar binary mixture of the two gases in EUO, the propane desorption peak is found to occur at a substantially higher temperature (75 °C) and the toluene desorbs at 70 °C, as shown in figure 2.

Thus, this experiment demonstrates that using zeolite samples like EUO with one-dimensional channels it is possible to trap the light hydrocarbon molecules up to higher...
temperature. No such effect has been observed for NaZSM-5 zeolite which has a three-dimensional pore-network connectivity. This shows that the presence of single-file diffusion is primarily responsible for the trapping effect observed in the experiment.

2.2. Lattice gas modeling

We model the narrow pore of EUO by a one-dimensional lattice whose ends are open. The diffusion of propane and toluene in the pore is modeled by a two-component symmetric exclusion process (SEP) where hard-core particles of two different species move on a lattice of \( L \) sites [8]. Propane and toluene molecules are represented as A and B particles, respectively. An A (B) particle can hop to the nearest neighbor site in either direction with rate \( w_A \) (\( w_B \)) if the destination site is empty. Thus the particles have a hard-core exclusion among themselves. At a boundary site of the lattice the A (B) particles can exit the system with rate \( w_A \) (\( w_B \)). Note that in this model we do not consider any additional energy barrier for desorption. Bulk diffusion and boundary desorption occur with the same rate. In figure 3 we have shown the possible dynamical moves of the model [2].

In this model we do not allow for boundary injection, i.e., once a particle hops out of the lattice from a boundary site, it is immediately removed from the system; no particle is allowed to enter the lattice through the boundary. Such a boundary condition resembles the experimental scenario where after the initial loading no more molecules are loaded into the zeolite sample in the course of the TPD measurement.

To model the temperature programmed desorption carried out in the experiment, we increase the temperature \( T \) in our model uniformly with time with a heating rate \( \lambda \) such that

\[
T(t) = T_0 + \lambda t. \tag{1}
\]

The hopping rates are assumed to have an Arrhenius dependence on temperature:

\[
w_A = \Gamma_A \exp(-E_A/kT) \quad w_B = \Gamma_B \exp(-E_B/kT) \tag{2}
\]

where \( k \) is the Boltzmann constant and \( T \) is the time-dependent temperature in (1). In our model the B particles are assumed to be heavier and more strongly adsorbed. This means that the activation energy for diffusion is larger for B particles, i.e., \( E_B > E_A \). As shown below, we set the overall time scale such that \( w_A \) and \( w_B \) are always less than unity. As a result, these rates can be directly interpreted as probabilities for Monte Carlo simulations. Notice that for single particles the hopping rates multiplied with the square of the lattice constant are equal to the diffusion constants of these particles. Therefore we refer to these rates also as diffusivities.

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In the two-component SEP with time-dependent hopping rates described above it is difficult to carry out any analytical calculation. In the case of time-independent rates, it is possible to describe the time evolution of the density profile using a set of coupled non-linear differential equations [9, 10]. However, for time-dependent rates, this Maxwell–Stefan type of approach can be used only if the system is in local equilibrium, which we find hard to justify for the experimental scenario of [1]. So we studied the system in [2] using dynamical Monte Carlo simulation. However, in the case of single-component loading, i.e., when only one species of particles is present on the lattice, it is possible to solve the system exactly and obtain a closed form expression for the desorption profile [7].

Let \( \rho_x(t) \) denote the average occupancy at site \( x \) at time \( t \). The time evolution of \( \rho_x(t) \) is governed by the diffusion equation on a lattice [11]:

\[
\frac{\partial \rho_x(t)}{\partial t} = w_\alpha(t)(\rho_{x+1}(t) + \rho_{x-1}(t) - 2\rho_x(t))
\]

where \( w_\alpha(t) \) is the time-dependent diffusivity as defined in (2) with \( \alpha \) being either A or B, depending on which species is present. In order to solve this lattice diffusion equation, we reparameterize time as \( d\tau = w_\alpha(t)dt \). In terms of this reparameterized time \( \tau \) the above equation becomes an ordinary diffusion equation without any explicit time-dependence in the diffusivity. This can be solved by using the ansatz

\[
\rho_x(\tau) = \sum_k (A_k(\tau)e^{ikx} + B_k(\tau)e^{-ikx})
\]

where \( A_k \) and \( B_k \) are constants that depend on the boundary conditions and the initial density profile.

Since there is no boundary injection into the lattice, we use the boundary condition \( \rho_x(\tau) = 0 \) for \( x = 0, L \). The solution then turns out to be

\[
\rho_x(\tau) = 2 \sum_{n=1}^{(L-1)/2} A_n \exp \left[ -2\tau \left( 1 - \cos \frac{(2n + 1)\pi}{L} \right) \right] \sin \frac{(2n + 1)\pi x}{L}
\]

where the value of \( \tau \) can be obtained by numerically performing the integration \( \int_0^\tau dt w_\alpha(t) \). The choice of initial condition determines the constant \( A_n \). We consider a homogeneous initial condition \( \rho_x(0) = \bar{\rho} \), for the bulk sites \( x \neq 0, L \). This is based on the assumption that in the experiment, when the zeolite samples are loaded with hydrocarbon molecules, the loading procedure gives rise to a uniform equilibrium bulk density. Such an initial condition yields

\[
A_n = \frac{1}{2} \bar{\rho} L \sum_{x=1}^L \sin \left( \frac{(2n + 1)\pi x}{L} \right).
\]

The instantaneous desorption current \( J_\alpha(t) \) is then given by \( w_\alpha(t)(\rho_1(t) + \rho_{L-1}(t)) \), which can easily be evaluated using the relations (5) and (6) [7].

Before we present our results, a brief discussion about the choice of parameters is in order. The typical channel length of an EUO zeolite is a few \( \mu m \) which is about a few thousand times the size of the diffusing hydrocarbon molecules. For computational simplicity, we work with a lattice size \( L = 1000 \). Also, in our calculations, we use the same temperature range 27–150°C as was considered in the experiment and have

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chosen the activation energy $E_A$ and the heating rate $\lambda$ such as to obtain a desorption peak within this temperature range. We have used an increment rate $\lambda = 10^{-5}$ degree per unit time to ensure that the current drops to zero at the final temperature, as in the experimental setting. When only A particles are diffusing on the lattice, we use $E_A = 116.3$ kJ mol$^{-1}$. The factor $\Gamma_A$, which sets the time scale, has been given a large value such that the variation of $w_A$ in the above temperature range is substantial which, as will be shown below, is necessary to reproduce the experimental data. This is ensured by setting $\Gamma_A = \exp(E_A/kT_f)$, where $T_f$ is the final temperature. We present our result for $J_A(t)$ in figure 4. In the same figure, the desorption profile for the single-component loading of B particles is also shown, with $E_B = 133$ kJ mol$^{-1}$, and $\Gamma_B = \exp(E_B/kT_f)$. Note that the desorption peak for $J_B(t)$ is at a higher temperature than that for $J_A(t)$. In other words, B is more strongly adsorbed than A, as expected. Note that $E_A$ in this case is not a truly physical quantity and its value depends on the details of the modeling approach.

Our calculation yields a desorption profile whose shape is similar to that seen in experiment. As temperature increases, the diffusivity grows and as a result $J_A(t)$ also rises. On the other hand, since there is no boundary injection, the lattice starts getting depleted of particles and after attaining a peak, $J_A(t)$ falls off. However, as shown in figure 4, the desorption peaks in our model occur at temperatures that are far too high: in the experiment, single-component propane and toluene peaks for EUO occur at 40 and 80°C, respectively [1]. It is possible to change the peak position in our model by changing $\lambda$ and $E_A$. A smaller $\lambda$ and/or a smaller $E_A$ would shift the peak towards lower temperature values. However, this would also change the qualitative features of the profile. One can show that if the values of $\lambda$, $E_A$ are reduced, $J_A(t)$ starts from a large value and undergoes

Figure 4. Variation of the instantaneous desorption current computed using equations (5) and (6) as a function of temperature (in °C) for single-component loading.
an initial drop before it peaks again at the desorption temperature. Such an effect is not observed in the experimental desorption profile. Thus it is not possible within this model to obtain a quantitative agreement with the experimental desorption temperature.

3. The desorption barrier and the peak position

Let us now consider which physical mechanism is missing to allow for a realistic desorption temperature. This mechanism must be such that the above mentioned initial fall in the current is suppressed, while the peak can be moved to the left. We suggest that this can be achieved by choosing a higher activation energy for the exit rate at the boundary. In other words, the particles undergo an activated diffusion in the bulk of the lattice with an activation energy $E_\alpha$, as before, but the desorption from the boundary is associated with a higher activation energy $V_\alpha$.

The presence of a higher activation energy near the exit of a zeolite pore has been reported in earlier studies involving molecular dynamics simulations [5, 6, 12]. The importance of such a surface energy barrier for the diffusion of adsorbed molecules inside a zeolite channel was studied in [5]. The diffusion of methane molecules inside the narrow pore of AlPO$_4$-5 zeolite was studied in the presence of a desorption barrier at the pore exit, using molecular dynamics simulations. It was found that the effect of this pore-exit barrier becomes less and less pronounced as the loading (i.e., the initial density of methane molecules inside the pore) is increased. This was explained by considering the attractive interaction between the molecules which gives rise to local clustering. Such clusters are often stable and the energy barrier for cluster diffusion is often lower than that for single-molecule diffusion [13]. It was argued in [5] that near the pore exit the desorption of a molecule into the gas phase is aided by the neighbors behind it, pushing it over the energy barrier, and thus effectively reducing the activation barrier for desorption. However, at low loading the molecules are too far apart and the escape of one sorbate molecule is unaffected by the presence of other molecules. Therefore, a molecule can exit the pore only when it has gathered enough momentum to jump over the energy barrier at the pore exit.

In our modified model we implement the desorption barrier as follows. A particle diffuses in the bulk with a rate $w_\alpha = \Gamma_\alpha \exp(-E_\alpha/kT)$, and it jumps out of the system at the boundary site with a rate $X_\alpha = M_\alpha \exp(-V_\alpha/kT)$, where $V_\alpha > E_\alpha$. As before, the pre-factor $M_\alpha$ is chosen such that the desorption rate changes over a substantial range in the experimental temperature range. This is ensured by choosing $M_\alpha = \exp(V_\alpha/kT_f)$, where $T_f$ is the final temperature. The other rules remain the same as before.

In the presence of a single component, with two different rates for bulk diffusion and boundary desorption, the time evolution of the local density $\rho_x(t)$ at the bulk is governed by the equation

$$\frac{\partial \rho_x(t)}{\partial t} = w_\alpha(t)(\rho_{x+1}(t) + \rho_{x-1}(t) - 2\rho_x(t)) \quad x \neq 1, L. \tag{7}$$

At the boundary one has

$$\frac{\partial \rho_1(t)}{\partial t} = w_\alpha(t)(\rho_2(t) - \rho_1(t)) - X_\alpha(t)\rho_1(t) \tag{8}$$

$$\frac{\partial \rho_L(t)}{\partial t} = w_\alpha(t)(\rho_{L-1}(t) - \rho_L(t)) - X_\alpha(t)\rho_L(t).$$
Note that in the above equation, the boundary densities couple with the new desorption rate \( X_\alpha \). In equations (7) and (8) it is not possible to remove the explicit time dependence of both \( w_\alpha \) and \( X_\alpha \) by performing a single scaling transformation on the time variable, as was done in section 2. Therefore, a solution in closed form similar to equation (5) cannot be obtained for this case. In order to solve the above set of equations numerically, we write them in the compact form

\[
\dot{\tilde{\rho}}(t + \delta t) = \mathcal{D}(t)\tilde{\rho}(t)
\]

(9)

where \( \delta t \) is an infinitesimal increment in time and the \( \tilde{\rho}(t) \) is a column vector, defined as

\[
\tilde{\rho}(t) = \begin{pmatrix}
\rho_1(t) \\
\rho_2(t) \\
\rho_3(t) \\
\vdots \\
\rho_{L-1}(t) \\
\rho_L(t)
\end{pmatrix}.
\]

(10)

\( \mathcal{D}(t) \) is the ‘transfer matrix’, given by

\[
\mathcal{D}(t) = \begin{pmatrix}
1 - X_\alpha(t) - w_\alpha(t) & w_\alpha(t) & 0 & 0 & \cdots & 0 & 0 \\
w_\alpha(t) & 1 - 2w_\alpha(t) & w_\alpha(t) & 0 & \cdots & 0 & 0 \\
0 & w_\alpha(t) & 1 - 2w_\alpha(t) & w_\alpha(t) & 0 & \cdots & 0 \\
\vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \vdots \\
0 & 0 & \cdots & \cdots & \cdots & \cdots & 0 \\
0 & 0 & \cdots & \cdots & \cdots & \cdots & 0
\end{pmatrix}.
\]

(11)

Starting from an initial condition \( \tilde{\rho}(0) \), it is then possible to obtain the density profile at time \( t \) by repeatedly applying (9). As explained in section 2, we choose a homogeneous initial condition. Using the resulting time-dependent local density profile \( \rho_x(t) \) we compute the instantaneous desorption current \( J_\alpha(t) = w_\alpha(t)(\rho_1(t) + \rho_{L-1}(t)) \). We adjust the parameters \( \lambda, E_\alpha \) and \( V_\alpha \) such that the peak of \( J_\alpha(t) \) is now placed close to the experimentally observed temperature. We present our plot of \( J_\alpha(t) \) as a function of temperature in figure 5.

Therefore, including the boundary effect in the form of a desorption barrier, we can find good quantitative agreement with the experimental desorption temperature for single-component loading. Note that to compute the desorption profile in this case, we did not have to do time-consuming Monte Carlo simulations. The quantitatively correct desorption profile was obtained by carrying out an exact numerical integration of (7) and (8). This computational advantage enables us to freely explore the various parameter regimes in our model. The position of the peak is sensitive to the choice of these parameters—a large value of the energy barriers shifts the peak position to higher temperature, as seen from the two curves presented in figure 5. The choice of \( \lambda \) also affects the desorption profile. A large value of \( \lambda \) means a fast increase in the diffusivity and as a result the current shows a rapid growth as a function of \( T \) and the effect of the depletion (see section 2) is not felt until higher temperature is reached, when the current falls off quickly. Thus a choice of large \( \lambda \) yields a higher desorption temperature. We verified this in calculations not presented here. On the other hand, similar calculations show that a too small \( \lambda \) brings about a qualitative change in the profile by introducing

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Figure 5. Instantaneous desorption current as a function of temperature (in °C) for single-component diffusion with a desorption barrier. We have used $L = 1000$, $\lambda = 5 \times 10^{-5}$ °C per unit time, $E_A = 1.6$ kJ mol$^{-1}$, $V_A = 68.1$ kJ mol$^{-1}$, $E_B = 33.2$ kJ mol$^{-1}$, $V_B = 99.8$ kJ mol$^{-1}$.

an initial decay in the current, as discussed in section 2. Note that $\lambda = 0$ corresponds to the equilibrium case where the diffusivity does not change with time. For such a case one expects an exponential decay of the desorption current as a function of time. The low temperature decay of the desorption current for very small $\lambda$ is nothing but a remnant of this equilibrium behavior.

4. Dynamical Monte Carlo simulation for the two-component loading

In this section we discuss the case where a binary mixture of A and B particles are diffusing on the lattice. For this two-component case we perform dynamical Monte Carlo simulations for measuring the TPD profile. We start with a homogeneous density profile, which is based on the assumption that the loading procedure in the experiment would generate uniform density inside the EUO pore.

Each Monte Carlo time step consists of $(L+1)$ update trials. During each such update trial a lattice bond is chosen uniformly at random. If the bond lies in the bulk, then the occupancies of the adjacent sites are updated following the rules described in section 2.1. If the bond lies at the boundary and the adjacent boundary site is occupied by an A (B) particle, then the boundary site is emptied with probability $w_A$ ($w_B$), with jump rates now understood as dimensionless jump probabilities for one jump attempt. More details on the simulation procedure have been given in [2].

In our earlier work without a desorption barrier our simulations showed that the presence of B particles does indeed raise the desorption temperature for the A component. The desorption temperature for A in the binary mixture is substantially higher than that
for the single-component case, as reported in the experiment. This shows that the strongly adsorbed B particles can successfully trap the weakly adsorbed A particles. However, at low temperature, some A particles are still found to escape. We have shown in [2] that this loss can be prevented by starting with an initial condition where no untrapped A particles are present near the boundary of the lattice.

A closer examination of the experimental data (figure 2) reveals that near the desorption peak the propane current is slightly higher than the toluene current. However, within a strict single-file condition this would not be possible. If the propane molecules can desorb only after the toluene molecules have desorbed, it is not possible to obtain a larger propane peak for an initial loading with an equimolar mixture. Therefore, to explain the experimental observation, we had to slightly relax the single-file condition by allowing ‘crossing events’ as shown in figure 6 (see [2] for details). In this relaxed single-file environment we retrieve an A current higher than the B current near the peak (see figure 7).

Now let us see what happens when the effect of the desorption barrier is included in the model. Since our earlier study reveals that some violation of the single-file condition takes place inside the channels, we carry out our simulation in a ‘relaxed’ single-file environment as in [2]. The simulation procedure remains essentially the same but the desorption now takes place with the modified rate $X_\alpha$. We present our data in figure 8.

The main observation is that we find a propane peak larger than the toluene peak as in the experiment. Secondly, both peaks occur at 70°C which is close to the experimental value, suggesting that our boundary desorption barrier approach, along with weak violation of the single-file condition, captures the major physical mechanisms that determine the diffusion and desorption of the binary mixture of molecules.

Further comparison between the experimental data in figure 2 and our results in figure 8 shows that not all of the aspects of the experimental data are captured within our model. The experiment shows that the presence of toluene strongly dominates the desorption process of propane but their profiles do not become identical. One can see that the toluene desorption takes place over a wider temperature range than that of
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Figure 7. Desorption profile for A and B with a relaxed single-file condition and without a desorption barrier. We have used $E_{AB} = 183$ kJ mol$^{-1}$ and $\Gamma_{AB} = \exp(E_{AB}/kT_f)$. The other parameters remain the same as in figure 4.

Figure 8. Desorption profile of A and B with a relaxed single-file condition and with a desorption barrier. We have used $E_{AB} = 83.1$ kJ mol$^{-1}$. The other parameters remain the same as in figure 5. Note that the inclusion of the desorption barrier strongly changes the position of the peak and now the peak is obtained at a temperature which is close to the experimental value.
propane. In our model we find that the tail of the profile for B does indeed stretch to higher temperature as seen in experiment. However, in contrast to the experimental observation, over a substantial range of temperatures the two profiles lie rather close, unlike in figure 2. In order to resolve this remaining discrepancy, one may have to take into account interactions between the molecules in more detail. As discussed in section 3, the interaction between the molecules gives rise to collective effects like concerted movement of molecular clusters [13]. It would be interesting to investigate whether some such effect is responsible for the relatively small width of the propane desorption profile observed in experiment.

5. Conclusions

We have attempted to describe the diffusion of hydrocarbon molecules in a narrow zeolite channel using the two-species symmetric exclusion process. Our earlier studies showed that using activated diffusion of hard-core particles on a lattice and assuming an Arrhenius dependence of the diffusivities on temperature one can explain the major qualitative features of the experiment [2]. However, this model was not appropriate for a quantitative comparison with the experiment data, as the desorption temperature obtained from this model was much higher than the experimental observation. In this paper, we have shown that in order to predict a realistic desorption temperature, one has to take into account boundary effects in the form of a desorption barrier: apart from an activated diffusion in the bulk of the lattice, the particles must overcome an additional energy barrier to desorb from the boundary. In a real system such a barrier comes from the attractive van der Waals interaction between the molecules and the pore wall.

The large energy barrier at the boundary has been found to have a strong influence for shorter zeolite channels [6]. A molecular dynamics study of the tracer exchange of guest molecules between a zeolite crystal and the surrounding gas phase shows that if the channel is short, then the desorption barrier gives rise to a flat density profile inside the channel. The appearance of a flat profile indicates that the equilibrium within the crystal is approached in a short time, compared to that needed to reach the concentration necessary to maintain equilibrium with the surrounding gas phase. Because of the large energy barrier at the pore exit, the system needs a long time to establish equilibrium with the surrounding gas phase. In [6] it was argued that when calculating the diffusion coefficients for short zeolite pores one should take into account the presence of such flat intra-crystalline density profiles. This could help to overcome the observed discrepancies with the diffusion coefficients obtained by microscopic methods. Our study shows that the desorption barrier is important also for long zeolite channels under non-equilibrium conditions since it changes significantly the desorption temperature in the TPD measurement.

From a modeling perspective we point out that the quantitative agreement between our Monte Carlo simulation results for the two-component case and the experimental data demonstrates that even without considering the details of the interactions present at the molecular level (as in molecular dynamics simulation) it is possible to explain the experimental results of [1] quantitatively with a good degree of accuracy. This suggests that adding simple coarse-grained interaction potentials would allow for a very detailed quantitative description of the experimental process. This is an important
conclusion because a molecular dynamics simulation method is computationally much more demanding than a Monte Carlo method and steady-state conditions are usually out of the range of accessibility of molecular dynamics simulations.

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