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Diffusion in a One-Dimensional Zeolite Channel: An Analytical and Numerical Study

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Abstract

Czaplewski *et al.* have demonstrated in an experiment that in the presence of strongly adsorbed hydrocarbon molecules inside a narrow, effectively one-dimensional zeolite channel, the effective desorption temperature of the weakly adsorbed hydrocarbon component is substantially increased. To explain their experimental data qualitatively, we propose a simple lattice gas model involving the diffusion of hard-core particles on a one-dimensional lattice. We present exact calculation and dynamical Monte Carlo simulations to show that taking into account an Arrhenius dependence of the single molecule diffusion coefficient on temperature, one can explain many significant features of the temperature programmed desorption profile observed in experiments.

1 Introduction

In a wide variety of chemical and petro-chemical processes, zeolites are used as catalysts and adsorbents for hydrocarbon molecules. In an automobile exhaust, zeolites are often used as hydrocarbon-traps. When an automobile engine is turned on, it needs a certain time (known as 'cold-start period') to reach its 'light-off' temperature, at which the hydrocarbon fuel may start burning. However, it is often found that a substantial amount of unburnt hydrocarbon fuel escapes into the atmosphere before the light-off temperature has been reached. This loss of fuel is known as cold start problem. One possible solution to this problem is to use zeolites to trap the hydrocarbon molecules at low temperature and release them once the temperature is high enough that the combustion of fuel can take place. However, while this method can be successfully applied for heavy hydrocarbon molecules, the lighter ones still manage to escape into the atmosphere.

Heavy aromatic molecules are strongly adsorbed in the zeolite and consequently need a high temperature in order to desorb from the channel. On the other hand,

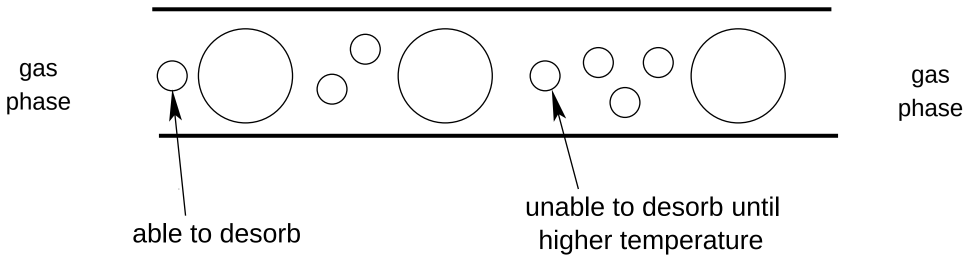

Figure 1: Schematic diagram of 1-d zeolite pore to show the trapping of light, less-strongly adsorbed molecules by heavier, more-strongly adsorbed ones.

light hydrocarbon molecules are weakly adsorbed and can easily desorb from the channel at relatively lower temperature. In [1] Czaplewski *et al.* have argued that if the zeolite channel is narrow enough, then the hydrocarbon molecules cannot pass each other inside the channel and the molecular transport takes place in essentially a single-file condition. In such effectively one-dimensional zeolite channels, the more strongly adsorbed heavy aromatic molecules block the motion of the less strongly adsorbed light hydrocarbon molecules, as shown in Fig 1. As a result, the light hydrocarbon molecules can desorb only after the aromatic molecules have desorbed which occurs at a higher temperature. Thus it was demonstrated in [1] that using a one-dimensional zeolite channel it is possible to raise the effective desorption temperature of light hydrocarbon molecules in the presence of large aromatic molecules.

Czaplewski *et al.* have performed an experiment using several zeolite samples with varying pore dimensionality and studied the desorption profile of propane (light hydrocarbon) and toluene (heavy aromatic molecule) mixture as the temperature is varied [1]. In conformity with the argument presented in the previous paragraph, they have found that in presence of toluene inside a one-dimensional zeolite channel, propane desorbs at a significantly higher temperature. However, no such effect has been observed for a zeolite with a three dimensional connectivity. This may be regarded as an experimental verification that single-file diffusion is responsible for hydrocarbon trapping as described above.

In a recent study, we have attempted to explain the above experimental observation using a simple lattice gas model [2]. Before we state our main results and present the scope of this paper, a few words on modeling transport inside zeolites is in order. Several different approaches have been used earlier to model such transport phenomena which include molecular dynamics simulations, dynamical Monte Carlo simulation, transition-state theory and Maxwell-Stefan approach [see [3] for a detailed review on this subject]. For the time-scales and length-scales that we are interested in, the method of dynamical Monte Carlo simulation is the most suitable approach. To this end we follow the strategy of modeling diffusion in zeolites as introduced by Kärger *et al.*[4, 5]. In the context of investigating so-called "molecular traffic control" [6] they used dynamical Monte Carlo simulation of a stochastic lattice gas model for zeolite systems with a network of perpendicular sets of intersecting channels (see [7, 8, 9] for recent progress along these lines).

In [2] we have modeled the narrow pore of a zeolite using a one-dimensional lattice and the hydrocarbon molecules as set of hard-core particles diffusing on that lattice. Our dynamical Monte Carlo simulations show that within this simple model, it is possible to explain the major features of the experimental data qualitatively. In this paper, we give a detailed review of our earlier simulation results in [2]. We also include a description of analytical calculation that we have been able to perform in certain cases.

2 1-d Zeolites as Hydrocarbon Traps: Experiment of Czaplewski *et al.*

Czaplewski *et al.* have performed experiments with several different zeolite samples with different pore sizes and various pore network connectivity. As an example of zeolites with one-dimensional channel, they studied EUO and Na-MOR and these data were compared against the data obtained for Na-ZSM-5, which is a zeolite with three-dimensional connectivity. In this section, we briefly summarise the features of this series of experiments relevant for our study.

The zeolite samples were loaded with equimolar binary mixture of propane and toluene and, for reference purpose, also with single-component propane and toluene separately. After the loading process was over, the whole system was purged in pure helium to ensure that no hydrocarbon molecules remain in the gas phase (see Fig 1). Then the temperature programmed desorption (TPD) was carried out where the sample was heated at a constant rate and the outflow was monitored using a flame ionisation detector and also a mass spectrometer.

For the single-component loading, the output current increases with temperature, attains a peak and then falls off. The desorption temperature of each component was measured at the position of the peak. For the one-dimensional zeolite Na-MOR, the desorption profile of single-component toluene shows one small peak at lower temperature and one larger peak at higher temperature. This two-stage desorption of single-component toluene gives rise to a two-stage desorption for propane in the binary mixture. However, for the zeolite EUO, which also has a one-dimensional channel, desorption profile has a single peak. For this simplicity, we have considered only EUO in [2] and have attempted to explain its desorption features within our simple lattice gas model.

For EUO, the single-component propane desorption peak is found at 40°C and for single-component toluene the peak occurs at 80°C, toluene being more strongly adsorbed. For an equimolar binary mixture of the two gases in EUO, the propane

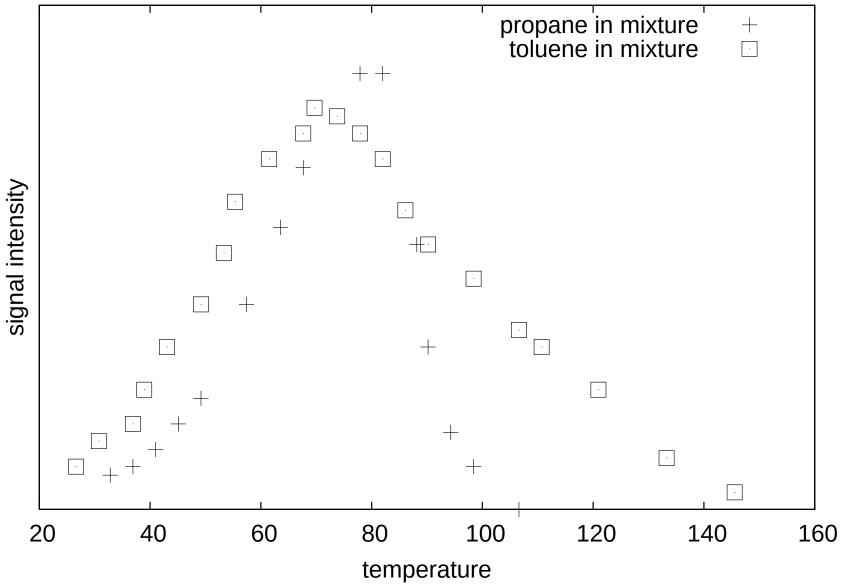

Figure 2: Experimental data for TPD profile of propane and toluene in binary mixture in zeolite EUO, as measured by Czaplewski *et al.* Data points taken from Fig 5 of [1].

desorption peak is found to occur at a substantially higher temperature (75°C) and the toluene desorbs at 70°C, as shown in Fig 2.

This experiment demonstrates that for a one-dimensional zeolite channel, it is possible to raise the effective desorption temperature of a light hydrocarbon molecule in presence of a heavier component. However, no such effect was found for the 3-d zeolite Na-ZSM-5, which is consistent with the absence of single-file diffusion in this material. In the next section, we describe the lattice gas model that we have used to explain the experimental data for EUO qualitatively.

3 Description of the Model

In the spirit of the approach by Kärger *et al.* [4, 5], we model the narrow pore of EUO by a one-dimensional lattice whose ends are open [2]. The diffusion of propane and toluene in the pore is modeled by two-component symmetric exclusion process (SEP) where hard-core particles of two different species execute diffusion on the lattice. We denote a propane molecule by the symbol 'A' and a toluene molecule by the symbol 'B'. A site can either be occupied by an A particle or a B particle or can remain vacant (denoted by '0'). An A or B particle can jump with rate w_A

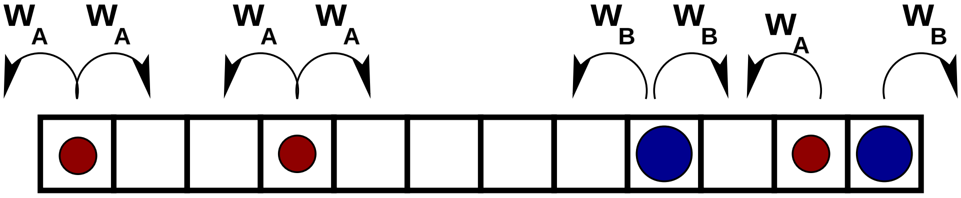

Figure 3: Two component SEP on an open lattice

or w_B, respectively, to the nearest neighbor site on either side, if the site is empty. If the neighboring site is occupied, no hopping is possible. The allowed moves are depicted in Fig 3. The dynamical moves in the bulk are:

$$\begin{aligned} A0 &\xrightarrow{w_A} 0A \\ 0A &\xrightarrow{w_A} A0 \\ B0 &\xrightarrow{w_B} 0B \\ 0B &\xrightarrow{w_B} B0 \end{aligned} \tag{1}$$

The A or B particles can exit through the boundary sites with rates w_A and w_B, respectively:

$$\begin{aligned} A &\xrightarrow{w_A} 0 \\ B &\xrightarrow{w_B} 0 \end{aligned} \tag{2}$$

Once they exit, they are removed from the system immediately and there is no boundary injection. Such a choice of boundary condition is actually motivated by the experiment in [1] where the zeolite channels are loaded before the start of TPD measurement and as temperature is increased, more and more hydrocarbon molecules desorb but no more are injected into the channel.

Eq. 1 defines a two-component SEP which describes the diffusion of two different species of hard-core particles. This system was earlier studied in [10, 11] for non-zero rates for boundary injection and extraction, and constant values of w_A and w_B. It was found that the equilibrium density profile is homogeneous, *i.e.* the probability that the i-th site contains an $A(B)$ particle is $\rho^{A(B)}$, where $\rho^{A(B)}$ refers to the reservoir density.

In our model, we consider time-dependent hopping rates w_A and w_B to model the TPD measurement carried out in experiment [1]. As time goes on, the temperature T of the system is changed at a constant rate:

$$T = T_0 + \lambda t \tag{3}$$

where T_0 is the initial temperature and λ is the increment in temperature per unit time. The jump rates w_A and w_B are assumed to have the following Arrhenius dependence on temperature:

$$\begin{aligned} w_A &= \Gamma_A \exp\left(-E_A/kT\right) \\ w_B &= \Gamma_B \exp\left(-E_B/kT\right) \end{aligned} \tag{4}$$

Here k is the Boltzmann constant. Since toluene is heavier, its diffusivity should be less than propane, *i.e.* $\Gamma_A > \Gamma_B$ and $E_A < E_B$.

Note that in this two-component SEP, hopping rates are explicitly time-dependent which makes this problem difficult to deal analytically. One might expect that for a very slow heating rate, one can use the same analytical tools as in [10, 11], where the rates were constant. However, such an approach assumes the presence of local equilibrium, which we find difficult to justify in this case. Hence in [2] we used dynamical Monte Carlo simulation to study the two-component system. However, when a single component is present, the local density follows a diffusion equation with a time-dependent diffusivity. For this case, it is possible to solve the system exactly and obtain a closed-form expression for the desorption profile, as shown in the next section.

4 Analytical Results for Single-Component Loading

When a single species, either A or B, is present, then the system executes a single-component SEP with time dependent rates. Let $\rho_x(t)$ denote the average occupancy at the site x, at time t. The time-evolution of $\rho_x(t)$ is governed by the diffusion equation on a lattice [12]:

$$\frac{\partial \rho_x(t)}{\partial t} = w_\alpha(t)\left(\rho_{x+1}(t) + \rho_{x-1}(t) - 2\rho_x(t)\right) \tag{5}$$

where $w_\alpha(t)$ is the time-dependent diffusivity as defined in Eq. 4 with α being either A or B, depending on which species is present. After rescaling time as $\mathrm{d}\tau = w_\alpha(t)\mathrm{d}t$, one can solve the above equation for $\rho_x(\tau)$, by using an ansatz of the form $\rho_x(\tau) = \sum_k \left(A_k(\tau)\exp(\mathrm{i}kx) + B_k(\tau)\exp(-\mathrm{i}kx)\right)$. Using the boundary conditions $\rho_x(\tau) = 0$ for $x = 0, L$, the solution turns out to be

$$\rho_x(\tau) = 2\sum_{n=1}^{(L-1)/2} A_n \exp\left[-2\tau\left(1 - \cos\frac{(2n+1)\pi}{L}\right)\right]\sin\frac{(2n+1)\pi x}{L} \tag{6}$$

where the value of τ can be obtained by numerically performing the integration $\int_0^\tau dt w_\alpha(t)$. The constant A_n is determined by the initial condition. Assuming that the loading procedure in the experiment generates a homogeneous equilibrium bulk density, $\rho_x(0) = \overline{\rho}$, we have

$$A_n = \frac{1}{2}\overline{\rho}L\sum_{x=1}^{L}\sin\left(\frac{(2n+1)\pi x}{L}\right). \tag{7}$$

The instantaneous desorption current $J_\alpha(t)$ is given by $w_\alpha(t)\,(\rho_1(t) + \rho_{L-1}(t))$, which can easily be evaluated using Eq. 6.

In our calculation, we use the same temperature range as considered in the experiment and have chosen the activation energy E_α and the temperature increment rate λ such as to obtain a desorption peak within this temperature range. However, as shown in Fig 4 below, the position of the desorption peak does not match with the experimentally observed value.

In the experiment diffusion of propane and toluene was studied inside an EUO pore. The amount of substance adsorbed inside an EUO pore depends on the details of the structure of the pore and the adsorbed species. In our model, we have not taken such details into account and have worked with an intermediate value of the density of A and B particles in the lattice. Note that the initial density $\overline{\rho}$ appears only as a prefactor in Eq. 7. So even if a different density value is chosen, there would be no qualitative change in the desorption profile. Also, the typical channel length of an EUO zeolite is 5 μm and the molecular diameters of propane and toluene are, respectively, ~ 4.4 Å and ~ 5.7 Å. The ratio of the channel length to the molecular size is ~ 1000, which should correspond to the number of lattice sites in our model.

Our calculation yields a desorption profile whose shape is similar to that seen in experiment. As temperature increases, diffusivity grows and as a result, $J_\alpha(t)$ also rises. But since there is no boundary injection, the lattice starts getting depleted of particles and after attaining a peak $J_\alpha(t)$ falls off. However, our calculation predicts a desorption peak which occurs at a temperature far too high. It is possible to adjust the position of the desorption peak by changing the two parameters λ and E_α in our model. A smaller λ and/or a smaller E_α would shift the peak towards lower temperature values but would also change the qualitative nature of the profile: $J_\alpha(t)$ would start from a large value and undergo an initial drop before it peaks again at the desorption temperature. Such an effect is not observed in the experimental desorption profile. Thus while trying to bring about a quantitative match with the experiment, we lose the qualitative agreement. Hence our present model is not fit for quantitative comparison with the experiment. So we aim to explain the main experimental results qualitatively (see section 6 for a discussion on quantitative comparison with the experiment). For this purpose, we work with a smaller lattice size for computational efficiency.

For numerical evaluation of the desorption current, we have used $L = 100$, $\overline{\rho} = 0.4$. Temperature is varied over the range of $27 - 150^\circ$C with the increment-rate $\lambda = 5 \times 10^{-4}$ degree per unit time. We have used $E_A = 83.1$ kJ/mol. The factor Γ_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. This is ensured by setting $\Gamma_A = \exp\left(E_A/kT_\mathrm{f}\right)$, where T_f is the final temperature. Such a choice also makes our simulation for the two-component SEP (see next section) more efficient. We present our result for $J_A(t)$ in Fig 4. In the same figure, the desorption profile for the single-component loading of B particles is also shown, with $E_B = 124.7$ kJ/mol, and $\Gamma_B = \exp\left(E_B/kT_f\right)$. Note that the desorption peak for $J_B(t)$ occurs

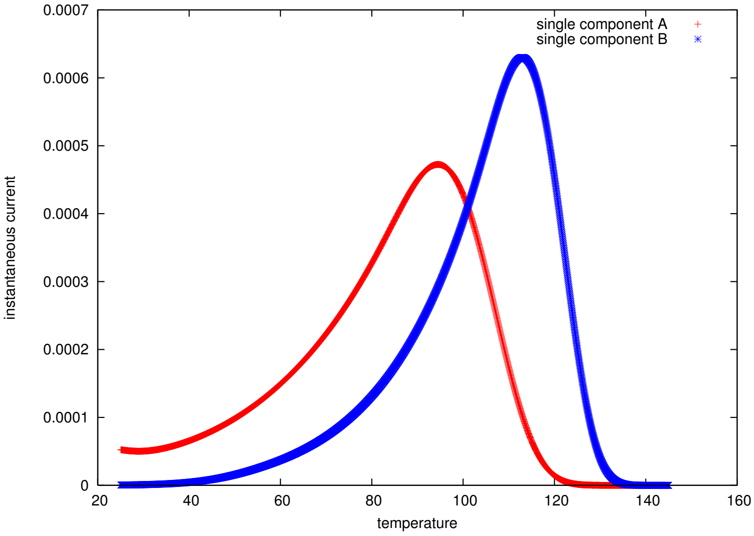

Figure 4: Variation of instantaneous current computed using Eq. 6 and 7 as a function of temperature (in °C) for single-component loading.

at a higher temperature than that for $J_A(t)$. In other words, B is more strongly adsorbed than A, as expected.

5 Simulation Results for Loading of Binary Mixture

As mentioned in section 3 the two-component SEP with time-dependent rates, cannot be treated analytically. In this section, we briefly review our main results of dynamical Monte Carlo simulations for the two-component case. For a description of our simulation method and other details see [2].

In the original experiment, zeolite samples were loaded with equimolar mixtures of propane and toluene. Likewise, we start with an initial configuration with $\rho_A = \rho_B$. We measure the number of particles of each species coming out through the boundary sites per unit time, as a function of temperature (or time). We call this quantity instantaneous current and denote it as $J_A(t)$ and $J_B(t)$. Starting with a uniform mixture of A and B, the plot of $J_A(t)$ and $J_B(t)$ is shown in Fig 5 against the variation of temperature (data earlier presented in [2]).

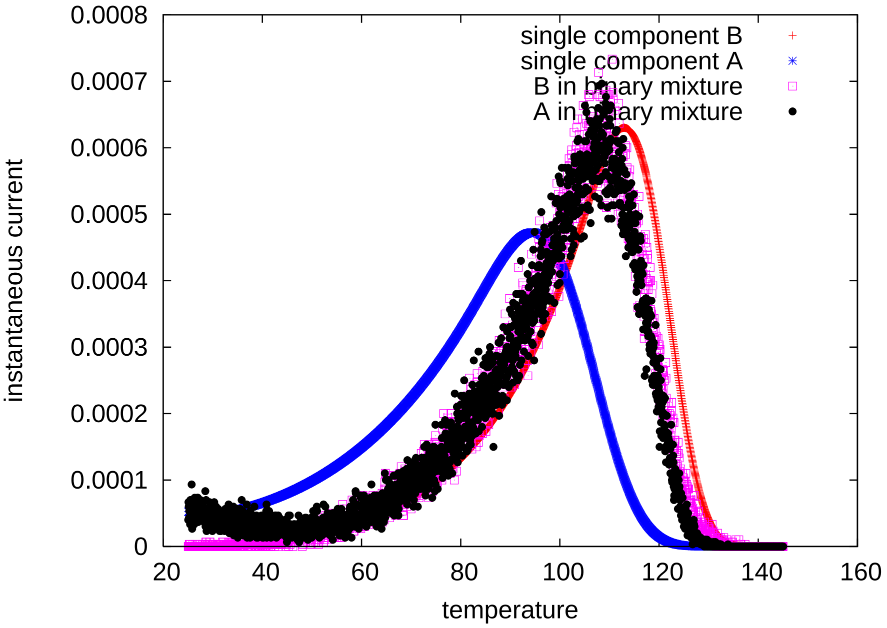

Figure 5: Plot of current vs. temperature (in °C) for a binary mixture of A and B. We have used $L = 100$, $\rho_A = \rho_B = 0.4$, $\lambda = 5 \times 10^{-4}$ °C per unit time, $E_A = 83.1$ kJ/mol, $E_B = 124.7$ kJ/mol, $\Gamma_A = \exp(E_A/kT_{\rm f})$ and $\Gamma_B = \exp(E_B/kT_{\rm f})$. The data has been averaged over 300,000 initial configurations. For comparison, single-component data presented in Fig 4 has been replotted.

As seen from the figure, the desorption temperature of B in binary mixture is close to the single-component peak. But the desorption temperature of A is significantly raised in presence of B, as seen in the original experiment. Note that even in the presence of B, a substantial number of A particles still desorb when the temperature is low. This happens due to the presence of untrapped A particles close to the boundary. We have verified that when all the untrapped A particles are removed from the initial configuration, the low temperature outflow of A is suppressed, as shown in Fig 6 [2]. Starting with an initial state with no untrapped A particles also resembles the actual experimental scenario. In the experiment, after the zeolite samples are loaded with the hydrocarbon mixture, the whole system was purged in pure helium to remove all traces of hydrocarbon molecules from the gas phase. However, it is also very likely that the weakly adsorbed propane molecules which are untrapped by toluene molecules and reside close to the boundary sites, are also purged out of the system at this stage, such that when the TPD measurement starts, there are no untrapped propane left in the system.

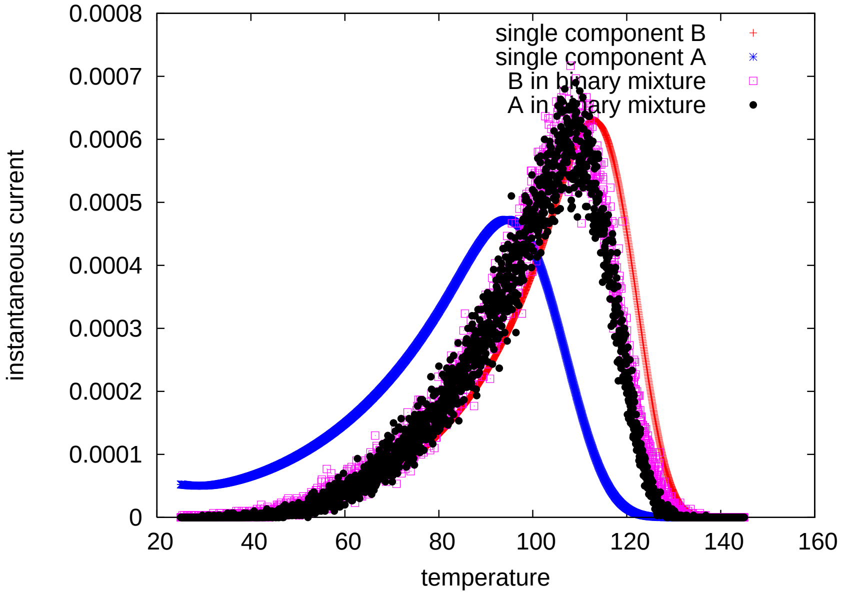

Figure 6: The low temperature outflow of A particles, as shown in in Fig 5 is suppressed when all untrapped A particles are removed from the initial configuration. The other simulation parameters are same as in Fig 5.

In [2] we have shown that our lattice gas model can qualitatively explain the main features of the experimental data. But on a closer scrutiny of the experimental data shown in Fig 2, we find that near the peak of the desorption profile the propane current is about 8% higher than the toluene current. However, in a strictly single-file condition, where propane molecules can escape only after the toluene molecules have desorbed, propane current can never exceed toluene current if we start from an equimolar mixture of the two. As discussed in [2], to reproduce this feature of the experimental data, we have slightly relaxed the single-file condition. In our model, we do so by allowing an A particle to diffuse past a B particle with a small rate w_{AB}, as shown in Fig 7. With a proper choice of w_{AB}, we obtain a desorption peak for A which is about 7% higher than that of B, close to the corresponding experimental value of 8% (see [2] for details).

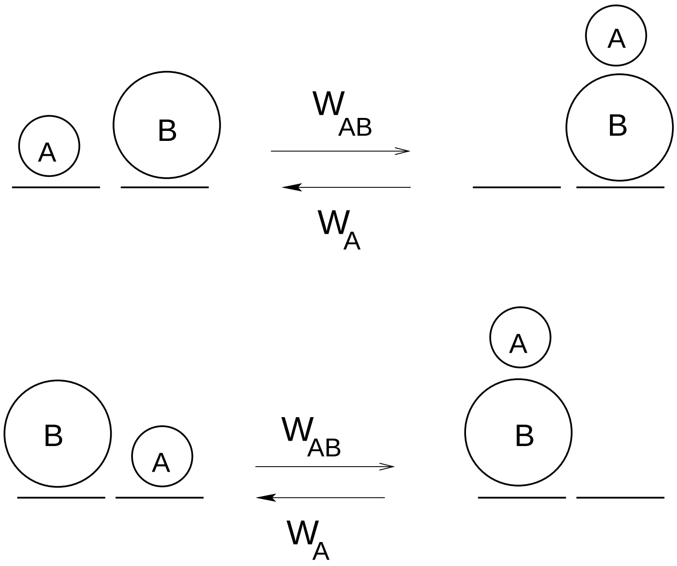

Figure 7: A particles can cross over B particles with a small rate when the single-file condition is relaxed.

6 Conclusion and Outlook

It is important to understand the transport mechanism of the molecules within the pores of zeolite in order to design more efficient applications for these materials. In this paper, we have considered an experiment involving diffusive transport of propane and toluene inside a narrow EUO channel. We model the EUO pore as a one-dimensional lattice and the diffusing molecules as two different species of hard-core particles, with two different diffusivities, moving on that lattice. This simple lattice gas model can explain the main experimental observations qualitatively. Within our model, it is possible to analytically compute the desorption profile for the case when only one species of particles is present. For the general two-component case, we performed dynamical Monte Carlo simulation.

Our model for two-component single-file diffusion shows that the presence of strongly adsorbed B particles raises the effective desorption temperature of weakly adsorbed A particles, as seen in the original experiment. This indicates that no detailed modeling of the interaction between the molecules or between the molecule and the pore-wall and boundary effects are required to explain the main experimental results qualitatively. Our Monte Carlo simulation shows that in order to reproduce a propane current larger than the toluene current, as seen in [1], one has to relax the single-file condition and allow the particles to cross each other for sufficiently high temperature. A violation of the single-file condition in zeolite channels has been found earlier while studying tracer diffusion of methane molecules in $AlP0_4$-5 zeolite using molecular dynamics simulation [13]. It was found that inside a narrow $AlP0_4$-5 pore, the methane molecules are not able to cross each other easily, but infrequent crossings do take place. So at large time, the signature of single-file diffusion is lost and the system behaves as in normal diffusion (see [13, 2] for more details).

Throughout, we have assumed that the diffusivities of the particles show an Arrhenius dependence on temperature. This may not hold true in general. In fact, violation of Arrhenius law was reported for certain zeolites in earlier studies [14]. However, to our knowledge, such behavior for EUO zeolite has not been reported.

Within our model, we do not find any strong qualitative dependence on initial density. This conclusion is open to experimental verification. Also, we have neglected any interaction between the molecules, except hard-core exclusion. From the qualitative agreement between our model and experiment, we conclude that the interaction details between the molecules do not play a crucial role. However, earlier studies have shown that these interactions can give rise to important collective effects [15] and hence might be relevant for a quantitative comparison with the experiment.

Finally, is it possible to obtain any quantitative agreement with the experimental data? We have seen before that even for the single-component loading, where it is possible to compute the current exactly, the desorption temperature does not match with that in the experiment. If we adjust λ and E_α to place the peak at the experimentally observed position, the desorption profile undergoes a qualitative change where the current starts from a large value and shows an initial decay with temperature. However, if it is possible to modify our model such that the above mentioned initial fall in the current is suppressed, while the peak can be moved to the left, then we might be able to obtain a realistic desorption temperature. We find that if we choose a higher activation energy for the exit rate at the boundary, then the low temperature current is suppressed and the desorption profile shows a single peak as before (detailed discussion in [16]). Thus by introducing the boundary effect in the form of an additional activation energy in our model, we can bring our desorption peak close to the experimental value. Earlier studies have shown that for many zeolites with narrow channels, the potential barrier for desorption from the marginal sites is larger than that for jumps between the neighboring sites [17]. It would be interesting to expermentally verify whether such boundary effects are indeed observed in diffusion of propane and toluene inside an EUO pore.

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