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Capturing the Concentration Dependence of *trans*-2-Butene Diffusion in Silicalite-2 Zeolite with a Jump Diffusion Model

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Molecular dynamics simulations of the diffusion of *trans*-2-butene in zeolite type MEL at 623 K have revealed an initial increase of the self-diffusivity with increasing loading, in contrast to simulation data collected for the other butene isomers. This is usually the signature of repulsive guest−guest interactions. At higher loadings, however, the concentration dependence was shown to decrease in a way consistent with attractive guest−guest interactions (Jousse, F.; et al. *J. Phys. Chem. B* **1997**, *101*, 4717). The initial rise reaches a maximum of about 25% for a loading of 1.5−2 molecules per unit cell. A jump diffusion model with parameters deduced from the molecular dynamics simulations accurately reproduces the diffusivity simulated at infinite dilution. For higher loadings guest−guest interaction parameters must be included in the jump diffusion model. Two simple models are presented, in order to rationalize the simulation results with a small number of parameters. The simpler model considers spherically symmetric adsorption sites and uses only two parameters; it is shown, however, that this model is unable to account for the simulated concentration dependence of the *trans*-2-butene self-diffusivity. The second model, with three parameters, includes the channel-like structure of the adsorption site and fits very effectively the concentration dependence of the diffusivity. Repulsive interactions between two molecules in the same site are responsible for the initial increase of the diffusivity. Attractive interactions arise when more than two molecules are in the same site, leading to a steeper decrease of the diffusivities with increasing loading.

1. Introduction

The importance of molecular transport in zeolites for catalytic and separation processes has long been recognized.[1] Although several experimental techniques have been developed for studying diffusion in zeolites,[2,3] their applicability is often limited and interpretation of the results can be difficult. Indeed, the observed diffusivities are controlled by a balance of attractive and repulsive host−guest and guest−guest interactions. Molecular modeling may provide a useful tool for disentangling these contributions. There are various levels of atomistic detail that can be incorporated into such modeling. Recently, we have reported the results of molecular dynamics simulations of the concentration dependence of *trans*-2-butene in silicalite-2.[4] In the present paper, we describe a coarse-grained model for these atomistic simulations, in an effort to reveal the physics essential to these transport phenomena.

The intracrystalline self-diffusivity is generally modeled using atomistic simulations and complex force fields, with either molecular dynamics[4−7] or Monte Carlo procedures coupled with transition-state theory.[8−17] Results of atomistic[11] or ab initio[18] simulations can also be used as input in lattice gas models, which are extremely useful for studying the influence of rare events.[19] Indeed, diffusion in zeolites is usually composed of infrequent jumps in a random walk.[2] Thus, atomistic simulations can provide the rate constants for random walk jumps, and rare events such as pore blocking can be incorporated easily in the model via other rate constants.[20] Moreover, the simplification introduced by the picture of diffusion as a jumping process often allows simple analytical expressions for the diffusivities, while retaining most of the physics of the processes.[21−27]

Diffusion of butene isomers in 10-membered ring zeolites might constitute an important component of the selectivity of these zeolites toward isobutene in butene skeletal isomerization.[7,24,28−30] In a previous paper,[4] we reported a study of the diffusion of butene isomers in zeolite types TON and MEL using molecular dynamics and a Monte Carlo jump diffusion model (JDM).[11,12] Although the energy barrier to diffusion in these all-silica zeolites was shown to be smaller than or on the same order as k_BT at 623 K, the molecular dynamics results could be interpreted in most cases on the basis of a jump diffusion process, either with or without correlations. The jump diffusion picture of transport in zeolites usually assumes that a molecule executes a series of jumps, with site residence times that are uncorrelated from one another during the random walk. This assumption holds when the relaxation time of a molecule at a given site is much smaller than the typical time between two jumping events. This is often interpreted as imposing the need for large energy barriers between adsorption sites. However, these assumptions are by no means necessary, and a jump diffusion model can include many kinds of correlations between particles or between events.[31]

Although these results were shown to hold for nonzero loadings,[4] the picture gets slightly more complicated because of guest−guest interactions. The exact dependence of the diffusivity upon concentration is a complex function of these

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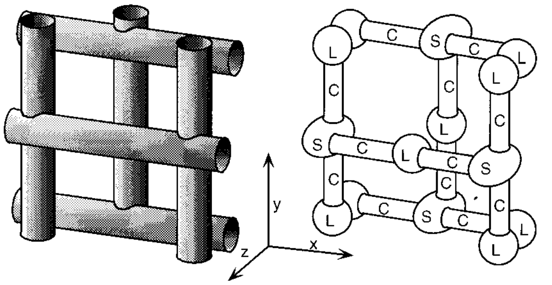

Figure 1. Sketch (left) of the channel system of zeolite MEL and (right) of the corresponding network of three sites (S), (L), and (C); only sites (L) and (S) were used as stable sites in the jump diffusion model of *trans*-2-butene diffusion in MEL.

interactions and of the network connectivity. For example, the diffusivity is generally reported to increase initially with increasing loading when the principal guest−guest interactions are repulsive and to decrease otherwise. At very high loadings the blocking of the channels lowers the diffusivity, regardless of the interactions. The molecular dynamics simulations reported in ref 4 revealed a general decrease of the self-diffusivity with increasing loading for isobutene, 1-butene, and *cis*-2-butene in silicalite-2 at 623 K, consistent with slightly attractive intermolecular interactions. On the other hand, *trans*-2-butene diffusivity showed a slight initial increase, up to about 2 molecules per unit cell, which would be the signature of repulsive guest−guest interactions. However, the simulations performed with up to 12 molecules per unit cell showed that the concentration dependence at higher loading, consistent with the other butene isomers, could be interpreted with only attractive interactions. Therefore, further study is necessary to confirm the simulated increase in the diffusivity and to resolve this apparent contradiction. Since we seek qualitative understanding of these effects, we develop below the simplest model consistent with our simulation results.

In this paper we present additional molecular dynamics calculations that give results consistent with the previous simulations. We show that a jump diffusion model is able to reproduce fairly well the dependence upon loading observed in the molecular dynamics simulations of *trans*-2-butene in silicalite-2. We also show that this dependence is consistent with a simple picture of guest−guest interactions. In the next section we outline the simulation methodologies used in this study, in section 3 we analyze the results, and in section 4 we conclude.

2. Simulation Methodology

Since the detailed methodology employed in this study has been described in a previously published paper,[4] this section gives a brief outline of the “computational experiments.” In this study, as in the previous one, we try to reduce the results of full atomistic simulations of the diffusion of *trans*-2-butene in silicalite-2 to its essential features by comparison with a jump diffusion model.

The structure of zeolite type MEL[32] builds a three-dimensional pore system from a single type of straight 5.3 × 5.4 Å channel running along the x and y directions shown in Figure 1. Two types of intersections connect these channels together: the smaller intersections involve roughly spherical cavities about 1.5 times the size of the channels; the larger intersections resemble small channels along z, since the distance between the centers of the intersecting channels is ca. 5 Å. Only the all-silica end member of the MEL family, corresponding to the material known as silicalite-2,[33,34] was considered. The previous study[4] showed that, as far as diffusion of butene isomers in this zeolite is concerned, the structure of MEL could be reduced to three types of sites shown in Figure 1: the large intersections (L), the small intersections (S), and the channel sites (C).

TABLE 1: Parameters Used in the JDM Model of *trans*-2-Butene Diffusion in Zeolite MEL at 623 K, Evaluated from the Molecular Dynamics Simulations at Infinite Dilution

parameter	
$4k_{SL}$ (10^{12} s^{-1})	0.107
$2k_{LS}$ (10^{12} s^{-1})	0.149
k_{LL} (10^{12} s^{-1})	0.200
max. number of molecules in site S[a]	4
max. number of molecules in site L[a]	1

[a] Evaluated from the MD runs at 20 and 23 molecules/simulation cell.

A. Molecular Dynamics. All molecular dynamics calculations were performed at 623 K (corresponding to the temperature of an optimized butene skeletal isomerization process in the zeolite ferrierite[35]), in a 20.5 × 20.5 × 27.5 Å^3 simulation cell consisting of 2 unit cells of MEL along [001]. The cff91_czeo force field of Biosym/MSI[36] was employed throughout; since only the all-silica zeolite was studied, electrostatic interactions were not included. All runs were performed in the *NVT* ensemble, using a 1 fs time step, keeping the zeolite lattice fixed but allowing the *trans*-2-butene molecules to be flexible. In this simulation cell, the dynamics of 1−23 molecules was followed using periodic boundary conditions. Owing to computer time limitations, the duration of the runs was varied between 200 ps for 1 molecule and 50 ps for 23 molecules. Several independent runs were performed to obtain converged statistical averages. The self-diffusivity was estimated using two independent methods: (i) from the mean-square displacement, using Einstein’s relation; (ii) from the velocity autocorrelation function;[37] see ref 4 for a more detailed description.

The site energies and the fundamental rates of the jump diffusion model were derived from the molecular dynamics simulations at infinite dilution. The sites are the most probable positions of the butene molecules during the molecular dynamic runs, which were found in this case to correspond to the channel intersections; these are energy maxima at 0 K but free energy minima at 623 K.[4] The rate constants were evaluated from the MD simulations using the relation: $k_{ij} = n_{ij}/t_i$, where t_i is the total residence time of a molecule in site i during the simulation and n_{ij} is the total number of crossings from site i to site j during the same time. The least likely molecular positions from the molecular dynamics runs were used as first approximations for the boundaries between the sites. The exact positions of the boundaries were further refined by minimizing the corresponding rate constants with respect to boundary locations. *trans*-2-Butene diffusion in zeolite MEL was shown to be accurately represented at infinite dilution by a jump diffusion process between only two of the three types of sites indicated in Figure 1: the intersection sites (S) and (L). Indeed, the system behaves as if the molecules do not reside in the channels but, rather, jump directly from one intersection to another.[4] The maximum number of molecules allowed per site was evaluated from the molecular dynamics simulations at very high loading (20 and 23 molecules/simulation cell.) All parameters directly evaluated from the molecular dynamics simulations are listed in Table 1.

B. Jump Diffusion Model. A jump diffusion model can represent *trans*-2-butene diffusion in silicalite-2 because the typical adsorption locations determined by molecular dynamics are well-described for all loadings by the lattice presented in Figure 1. All parameters for the jump diffusion model of *trans*-

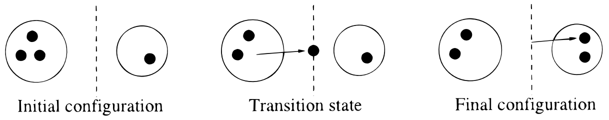

Figure 2. Sketch of a possible jump from an initial site 1 to a final site 2.

2-butene diffusion at infinite dilution were extracted from the molecular dynamics simulations. However, for nonzero loading, we need to include the effect of the molecule−molecule interactions. While it is possible to calculate the exact guest−guest interactions for a given configuration, we observe during the MD simulations an averaged quantity. Since we are looking more for qualitative understanding of these effects, our aim is to reduce the number of parameters that have to be adjusted in order to reach this agreement and to assign their physical meaning. In this section, we present and discuss this simple assignment based on transition-state theory.[8,9]

Transition-state theory asserts that the rate constant between two states with internal energy E_{init} and E_{final} separated by a transition state with internal energy E_{TS} can be written as:

$$k_{\mathrm{init}\rightarrow\mathrm{final}} = \nu^* \exp[-\beta(E_{\mathrm{TS}} - E_{\mathrm{init}})] \tag{1}$$

where ν^* is a "typical" frequency of the system that depends on the entropy of the particles in the initial site and at the transition state. This preexponential frequency typically ranges between 10^{11} and 10^{13} s^{-1} for the system under consideration[12] and varies much less with temperature than does the exponential term.

Model 1. Considering the system of two sites presented in Figure 2, the initial site contains i molecules and the final site j molecules. Let us define the following energies: ϵ_1 and ϵ_2 are the site energies of one molecule in site 1 and 2, respectively; ϵ_t is the energy of a molecule at the transition state; ϵ_{12} is the interaction energy between a molecule in site 1 and a molecule in site 2; ϵ_{1t} and ϵ_{2t} are the interaction energies between a molecule at the dividing surface and a molecule in site 1 and site 2, respectively. Finally, ϵ_{11} and ϵ_{22} are the interaction energies between two molecules, both in site 1 or in site 2, respectively. Please see Figure 3 (top) for a graphical representation of these energy terms. The difference between the energy of the transition state and that of the initial state for the 1 → 2 jump is then given by:

$$E_{\mathrm{TS}} - E_{\mathrm{init}} = [\epsilon_t - \epsilon_1] + (i-1)[\epsilon_{1t} - \epsilon_{11}] + j[\epsilon_{2t} - \epsilon_{12}] \tag{2}$$

Supposing that the number of molecules in a site does not have any influence on the preexponential factor, the rate constants can be written as

$$k_{12}(i, j) = k_{12}(1, 0)\alpha_1^{i-1}\beta_1^{j} \tag{3}$$

where we have introduced the physical parameters α_1 and β_1 defined by

$$\alpha_1 = \exp[-(\epsilon_{1t} - \epsilon_{11})/kT] \tag{4}$$

$$\beta_1 = \exp[-(\epsilon_{2t} - \epsilon_{12})/kT] \tag{5}$$

Clearly two other parameters α_2 and β_2 should be defined to describe the rate constants $k_{21}(i, j)$ using the same formal expression as eq 3.

These parameters α and β can be related to intermolecular interactions. We suppose that the molecule−molecule interaction potential has a simple Lennard-Jones form, as exemplified in Figure 3. Depending on whether the molecules are constrained to be close or not-so-close to each other inside one site, the parameter α can be larger or smaller than unity; $\alpha > 1$ indicates repulsive interactions between the molecules inside a site, while $\alpha < 1$ indicates attractive interactions. We found in ref 4 that the concentration dependence of 1-butene, *cis*-2-butene, and isobutene could be very well described by varying only one slightly attractive interaction parameter $\alpha < 1$ for these different molecules and by using for all molecules $\beta = 1.0$, that is, $\epsilon_{12} \approx \epsilon_{2t}$. Both ϵ_{12} and ϵ_{2t} correspond to a large distance, as compared to ϵ_{11}, the interaction between two molecules inside a site. That they are found to have the same value can be interpreted in two ways: either these interactions are nonzero, and therefore the intermolecular interaction must be long-ranged, or these interaction parameters are practically zero, and the total interaction must be short-ranged, indeed confined to molecules inside the same site. Since in the molecular dynamics calculations no long-ranged electrostatic interactions were used, it follows that only the second hypothesis is physically consistent with the simulations. Thus, the guest−guest interactions of 1-butene, *cis*-2-butene, and isobutene in MEL were found to be short-ranged and slightly attractive. Note that this reduces the present two-parameters model to a one-parameter model.

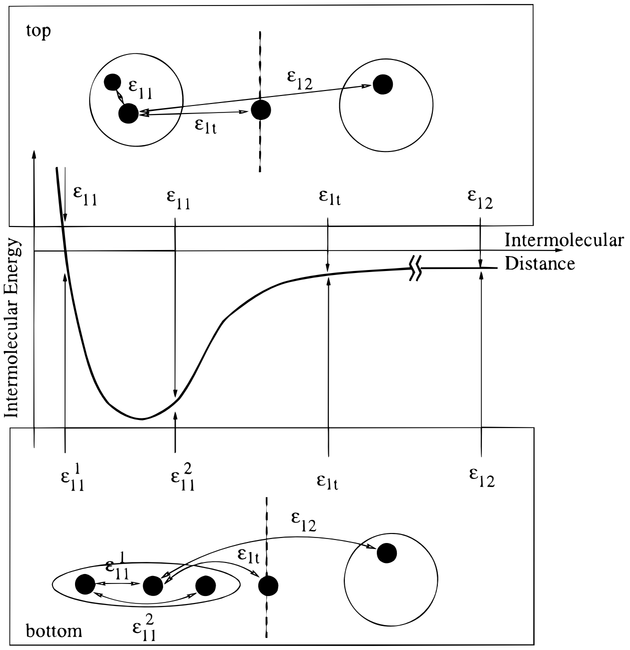

Figure 3. Example of a possible Lennard-Jones molecule−molecule interaction potential; the top drawing describes the various interaction energies in the case of the first and simpler model; the bottom drawing describes the meaning of the various interaction energies in the case of the second model, accounting for the channel-like shape of the adsorption site.

The case of *trans*-2-butene is slightly different. Indeed, an initial increase of the diffusivity with loading signals repulsive interactions at low loading, while at higher loading the decrease of the diffusivity is consistent with attractive interactions. It is clear that a one-parameter model cannot capture this behavior. In a first effort to understand the physics behind this behavior, we supposed that in the model presented above the interactions at the transition state and between two sites could be different and therefore explored the whole (α, β)-parameter space. We will see in the next section, however, that even this more general model cannot describe the concentration dependence of *trans*-2-butene in silicalite-2. It is therefore necessary to introduce a second model.

Model 2. Model 1 corresponds to the maximum degree of simplification: the sites are considered symmetric, so that all molecules sorbed inside a site experience the same site energy and interaction energy. The *trans*-2-butene molecules are initially sorbed at the channel intersections but fill in the channels as the concentration increases.[4] At high loading, we should account for the fact that the molecules are packed inside the channels of MEL. This breaks the symmetry of adsorption, requiring that we modify the guest−guest interactions as shown in Figure 3 (bottom) to reflect this anisotropy. We suppose that all molecules in a given site still have the same site energy ϵ_1 or ϵ_2; this is justified by the fact that we observe in the MD simulations averaged quantities. Sites labeled 1 have the channel-like structure sketched by an ellipse in Figure 3 (bottom), while sites 2 retain the spherical symmetry of the former model. This simplification is completely justified in our case since sites 2 correspond to sites (L), which can accommodate one molecule at most. Two molecules together in site 1 next to each other have the interaction energy ϵ_{11}^1; if they are separated by one other molecule, their interaction energy is ϵ_{11}^2. We will simplify further by assuming that all molecules that are not directly adjacent have this same interaction energy ϵ_{11}^2. Then, the rate constant $k_{12}(i, j)$ takes the following form

$$k_{12}(i, j) = \begin{cases} k_{12}(1, 0)\beta_1^j & \text{for } i = 1 \\ k_{12}(1, 0)\alpha_1\beta_1^j & \text{for } i = 2 \\ k_{12}(1, 0)\alpha_1\gamma_1^{i-2}\beta_1^j & \text{for } i > 2 \end{cases} \tag{6}$$

where β_1 has the same meaning as in eq 3, α_1 has been modified, and the new parameter γ_1 is introduced according to

$$\alpha_1 = \exp[-(\epsilon_{1t} - \epsilon_{11}^1)/kT] \tag{7}$$

$$\gamma_1 = \exp[-(\epsilon_{1t} - \epsilon_{11}^2)/kT] \tag{8}$$

It is clear from Figure 3 that if $\epsilon_{1t} < \epsilon_{11}^1$, so that $\alpha_1 > 1$, the initial interaction between two molecules is repulsive. On the other hand, ϵ_{1t} might be larger than ϵ_{11}^2 so that $\gamma_1 < 1$, and the total interaction energy between more than two molecules in the same site becomes attractive. We can now make a parallel with the the results found in the case of 1-butene, *cis*-2-butene, and isobutene as discussed in the previous section. Indeed, supposing that the interactions are short-ranged, that is, confined to molecules in the same site, leads to $\epsilon_{1t} \approx \epsilon_{2t} \approx \epsilon_{12} \approx 0$; in this case $\beta = 1.0$, and the three-parameter model reduces to a two-parameter model involving (α, γ)-parameter space.

3. Results and Discussion

A. Atomistic Simulations. The self-diffusivities calculated from the molecular dynamics simulations are presented in Figure 4. Open and filled circles denote the diffusivities estimated from the mean-square displacement (MSD) of the *trans*-2-butene center-of-mass (COM) and from the integration of the velocity autocorrelation function of the COM, respectively; the error bars correspond to the mean error calculated from the statistical averages. Also presented is the partial diffusivity along the *z* axis. The initial increase of the diffusivity with concentration of *trans*-2-butene observed in our previous simulations is confirmed: it reaches a maximum of about 25% for 1.5-2 molecules per unit cell corresponding to a relative concentration of about 0.125. The diffusivity along *z* does not show any increase with the number of molecules in the simulation cell. This observation is in good agreement with the parameters of the jump diffusion model (JDM) derived from the molecular dynamics simulations. Indeed, the diffusion along *z* proceeds partly via (L)→(L) jumps. Since these sites can only accommodate one molecule at most, the rate constant should not depend on the concentration through anything but a normal site-blocking model, which lowers the self-diffusivity when the concentration increases.

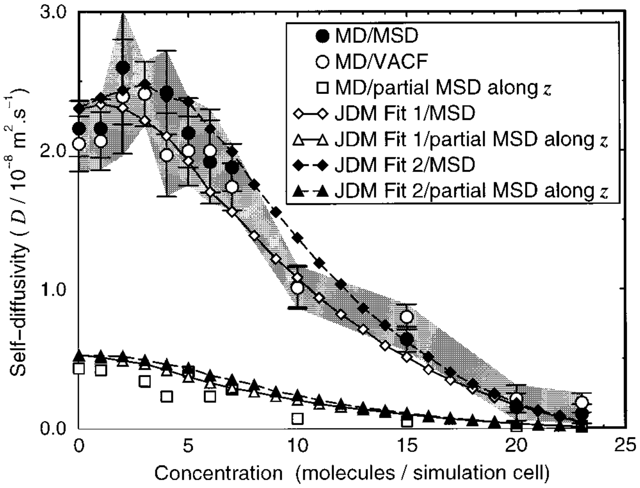

Figure 4. Self-diffusion coefficient of *trans*-2-butene in zeolite MEL at 623 K, as a function of the number of molecules sorbed per simulation cell. Keys to the legend: MD stands for molecular dynamics of *trans*-2-butene in MEL, using the cff91_czeo force field of Biosym/MSI; JDM stands for Monte Carlo jump diffusion model; MSD stands for calculation from the linear regression of the mean-square displacement; VACF stands for calculation from the integration of the velocity autocorrelation function. Both JDM fits use the parameters listed in Table 1 and eq 6, with the following interaction parameters: fit 1 ($\alpha = 2.0$, $\beta = 1.0$, $\gamma = 0.3$); fit 2 ($\alpha = 5.0$, $\beta = 1.0$, $\gamma = 0.2$). The grey shaded zone corresponds to the interval between the minimum and maximum possible values of *D* according to the MD simulations.

B. Coarse-Grained Modeling. *Model 1.* We were unable to find interaction parameters α and β that provide a satisfactory fit between the concentration dependence of the diffusivities from our MD simulations and those from the simpler model of guest−guest interactions. The reasons for this failure become apparent when we analyze the concentration dependence of diffusion emerging from this model. Figure 5 shows typical curves illustrating the qualitative behavior of the concentration dependence of diffusion for several values of the parameters α and β.

Spanning the whole (α, β)-parameter space using Monte Carlo simulations proves a rather cumbersome task. In order to help us explore how the first model of guest−guest interactions controls the concentration dependence of diffusion, we employed an analytical expression for the diffusivity as a function of the interaction parameters α and β.[25−27] Obtaining an analytical expression of the diffusivity for the network of sites depicted in Figure 1, however, is rather difficult. Therefore, we used a simplified version of the site network, consisting of a square lattice of identical sites that can be occupied by zero, one, or two molecules at the most. The procedure employed to determine the diffusivity within the mean-field approximation is indicated in the Appendix. The curves from the analytical model are plotted against the corresponding Monte Carlo simulations for the actual lattice of sites in Figure 5. We note that the analytical curves were scaled to reproduce the self-diffusivity for the silicalite-2 lattice of sites at infinite dilution. Therefore, the curves plotted in Figure 5 do not give any indication of the accuracy of representing the lattice of silicalite-2 by a two-dimensional square lattice. It is clear, however,

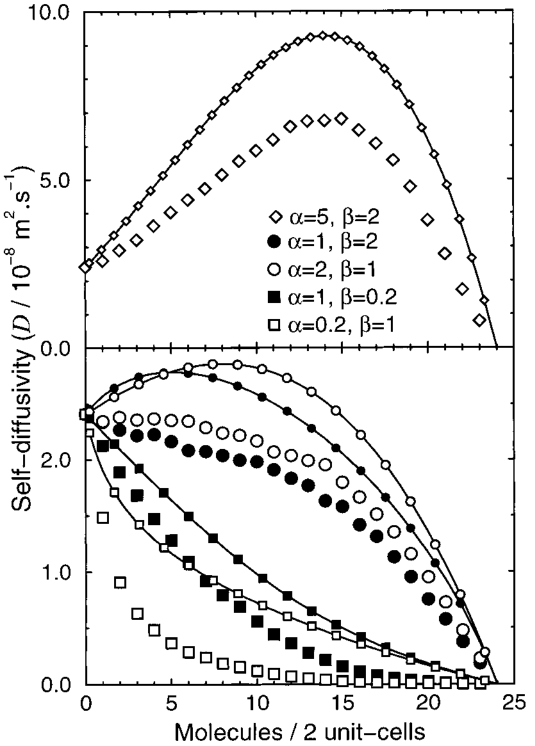

Figure 5. Symbols: Monte Carlo self-diffusivity of *trans*-2-butene in the model of silicalite-2 depicted in Figure 1, as a function of the concentration, using the simpler model of guest−guest interactions described in the text, for several values of the interaction parameters α and β. Lines + symbols: corresponding self-diffusivities calculated on the simplified square lattice depicted in Figure 6, using the mean-field approximation given in the Appendix.

that the concentration dependence of diffusion is qualitatively reproduced with this model of guest−guest interactions. We have thus utilized the analytical model to determine thoroughly how α and β control the concentration dependence of diffusion.

An initial increase of the diffusivity can only appear if $\alpha > 1$, that is, for repulsive interactions inside a site, and if $\beta \geq 1$, that is, repulsive or zero interaction between two sites. The initial increase of the self-diffusivity is damped out by the blocking of the sites, so that it tends to zero at high loading. We can see from Figure 5 that this damping is fully active only for rather high concentrations of molecules. The molecular dynamics simulations, on the other hand, reflect a steep decrease for already small to medium concentrations.

Model 2. Two examples of fits attempted with the second model of guest−guest interactions are presented together with the molecular dynamics results in Figure 4. With this physical model, it is possible to reproduce well the simulated behavior of the concentration dependence of *trans*-2-butene in MEL, both for total diffusion and for partial diffusion along the z axis. In all cases we found good fits using $\beta = 1.0$, showing that the interactions between *trans*-2-butene molecules are localized within a site; this is consistent with the other butene isomers.

The molecular dynamics results presented in Figure 4 suffer from rather large error bars because of the statistical uncertainties inherent to these atomistic simulations. Therefore, a number of possible fits of the molecular dynamics results are possible, two of which are displayed in Figure 4: fit 1 ($\alpha_1 = 2.0$, $\gamma_1 = 0.3$); Fit 2 ($\alpha_1 = 5.0$, $\gamma_1 = 0.2$). Since the simulations have been performed at 623 K, these values correspond to the interaction energies listed in Table 2. We note that the two fits presented in Figure 4 are not the only possible ones and that other satisfactory fits were obtained but are not displayed in Figure 4 for clarity. These other parameters included the following sets: ($\alpha = 10.0$, $\gamma = 0.1$); ($\alpha = 3.0$, $\gamma = 0.1$). In all fits $\alpha > 1$, $\gamma < 1$, and $\alpha\gamma \leq 1$. This region of parameter space leads to the following interpretation of the concentration dependence of the diffusivity of *trans*-2-butene in silicalite-2: a repulsive interaction between molecules inside the same sites (S) at low loading is compensated by attractive interactions in the same site at medium to high loadings. We note again that $\beta = 1.0$ means that long-ranged interactions between molecules at two different sites, or between a site and a transition state, are negligible.

TABLE 2: Interaction Parameters Used To Calculate the Fits of the Concentration Dependence of *trans*-2-Butene Diffusion in Silicalite-2 Presented in Figure 4

interaction	fit 1	fit 2
ϵ_{11}^{1}	+3.6 kJ·mol^{-1}	+8.3 kJ·mol^{-1}
ϵ_{11}^{2}	−6.2 kJ·mol^{-1}	−8.3 kJ·mol^{-1}
ϵ_{2t}, ϵ_{1t}, ϵ_{12}	0.0	0.0

The MD results reveal a qualitative difference in the concentration dependence of the diffusion of *trans*-2-butene in silicalite-2, as compared to the other butene isomers. The present analysis provides an interpretation of this difference in terms of guest−guest interactions and site symmetry. Isobutene, *cis*-2-butene, and 1-butene feel a symmetric interaction in MEL, with consistently attractive interactions inside one site. In the case of *trans*-2-butene the sites cannot be considered symmetric, and the nearest neighbors inside one site feel a repulsive interaction while the next-nearest neighbors feel an attractive interaction. It is not obvious why these interaction parameters should apply to *trans*-2-butene and not to the other butene isomers. While it is possible that the different molecular shapes of these isomers, when adsorbed in a channel zeolite, lead to different adsorption geometries and hence to different guest−guest interactions, much more study is required to justify this idea.

In order to pinpoint the precise region of parameter space, (α, γ), that well describes the *trans*-2-butene in silicalite-2, further MD simulations at other temperatures will be required. These calculations are presently under way.

4. Conclusion

It was shown in a previous work[4] that a jump diffusion model, with parameters extracted from molecular dynamics simulations, reproduces very well the self-diffusivity of butene isomers in zeolite MEL. At higher loading, however, it is necessary to include additional parameters to fit the simulated concentration dependence of diffusion. In the case of isobutene, 1-butene, and *cis*-2-butene, it was shown that a single parameter corresponding to slightly attractive interactions between the molecules could account for the observed concentration dependence, while this was not the case for *trans*-2-butene.

The molecular dynamics simulations presented in this article confirm the trends observed in previous simulations:[4] in contrast to the data collected for isobutene, *cis*-2-butene, and 1-butene, the self-diffusivity of *trans*-2-butene in zeolite type MEL at 623 K initially increases with increasing loading. This has been observed in many different guest−zeolite systems[2] and is generally the signature of repulsive guest−guest interactions.[38] However, the molecular dynamics simulations performed with up to 23 molecules per simulation cell showed that the concentration dependence of *trans*-2-butene self-diffusivity at high loading can be interpreted with a model using only attractive interactions.

We presented in this paper two simple models describing in a semiquantitative way the effect of the guest−guest interactions on the jump rate constants and thereby on the diffusivities. The first and simpler model considers the adsorption sites as spherically symmetric and uses only two parameters. Since the sites are spherically symmetric, all pairs of molecules inside the same site have the same interaction energy. We have shown, however, that this model does not account for the observed concentration dependence of the self-diffusivity. The second model accounts for the channel structure of the adsorption sites, albeit in a very simplified manner. In that case the interaction energy is different for different pairs of molecules sorbed in the same site, depending on whether they are directly adjacent or not. Exploiting two out of three adjustable parameters in this second model, we reproduce very well the concentration dependence of the diffusivity as determined by the molecular dynamics simulations. The corresponding interaction parameters have a physically reasonable value.

The apparent contradiction between repulsive interactions at low loading and attractive interactions at higher loading mentioned above is thereby resolved. Initially, pairs of molecules in the same site do present a small repulsive interaction. When more than two molecules are sorbed, an attractive interaction appears between molecules farthest apart, thus compensating the repulsive interactions and accounting for the rapid decrease of the diffusivity at medium to high loadings.

A molecular dynamics study of the temperature dependence of diffusion as a function of loading could also be interpreted by our jump diffusion model, since the parameters used in the model depend exponentially on inverse temperature. These calculations are presently under way and will be reported in a forthcoming publication.

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Appendix: A Simplified Expression for the Tagged Particle Diffusivity on a Square Lattice with Soft-Core Interactions

The generalized atomic hopping problem at lattice sites has been addressed a number of times in the literature.[39−41] It is generally a nontrivial problem even without considering multiple occupancies. The problem of multiple occupancies, however, arises particularly when considering diffusion in zeolites, since the cages provide natural sites that can be filled by several molecules;[38] "soft-core interactions"[42] clearly have to be included in these cases. The simple model presented in the body of this paper proposes to describe the effect of multiple occupancy on the site-to-site rate constant in an effective way, using only two parameters α and β. Although this simplified model can be straightforwardly studied by Monte Carlo simulations, it does not admit a simple analytical expression that could be used to study the systematic influence of the parameters. Therefore, we modified the network of sites in order to simplify the problem and obtain a tractable expression. We believe that this simplification, however, retains most of the physics of the actual system of interest.

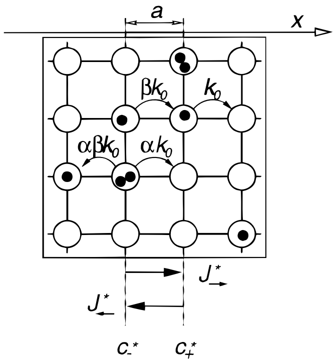

Figure 6. Square lattice model allowing double occupancy of the sites.

We consider, rather than the network of two different sites presented in Figure 1, a square lattice of side a composed of only one site. Each site can be filled with zero, one, or two molecules at most. The lattice of site is depicted in Figure 6. The rate constants $k(i, j)$ to jump from an original site containing i molecules to a final site containing j molecules can be written, in accordance with eq 3

$$k(1, 0) = k_0$$

$$k(1, 1) = \beta k_0$$

$$k(2, 0) = \alpha k_0$$

$$k(2, 1) = \alpha\beta k_0$$

We consider the flux of "tagged" particles along the x axis, J^*, between two successive columns of sites. We denote c^*_+ and c^*_- as the concentrations of tagged particles at the right-handed column and left-handed column, respectively. The total concentration of molecules in the lattice is constant and equals c. The self-diffusion coefficient along the x axis is defined by:[2]

$$J^* = -D_x \frac{\partial c^*}{\partial x}\bigg|_{c=\mathrm{const}} \tag{A1}$$

Since the total concentration of molecules remains constant throughout the lattice, the total flux of molecules equals zero. Therefore, the magnitude of the flux, J, moving to the right equals that moving to the left, i.e., $J = |J_\rightarrow| = |J_\leftarrow|$. Since the tagged particles are otherwise indistinguishable from the other particles, the flux of tagged particles moving to the right is given by the proportion of the flux, J, pertaining to tagged particles at the left column. Similarly, the flux of tagged particles moving to the left is the negative fraction of flux pertaining to tagged particles at the right column, i.e.

$$J^*_\rightarrow = \frac{c^*_-}{c} J$$

$$J^*_\leftarrow = \frac{c^*_+}{c} J \tag{A2}$$

The net total flux of tagged particles is then given by

$$J^* = J^*_{\rightarrow} + J^*_{\leftarrow} = \frac{c^*_- - c^*_+}{c} \qquad (A3)$$

A first-order Taylor expansion for the concentration of tagged particles gives

$$c^*_- = c^*_+ - \frac{\partial c^*}{\partial x}a \qquad (A4)$$

which then gives for the total flux

$$J^* = -\frac{a}{c}\frac{\partial c^*}{\partial x}J \qquad (A5)$$

Equations A1 and A5 show that the self-diffusion coefficient can be written as

$$D_x(c) = \frac{a}{c}J(c) \qquad (A6)$$

D depends on the total concentration of particles in the system but not on the concentration of tagged particles.

Let us denote p_0 as the probability that a site is empty, p_1 the probability that it is occupied by just one molecule, and p_2 the probability to be doubly occupied. c is the total total concentration of molecules in the system and C_S the concentration of sites. The flux of molecules along one direction $x+$ can be written as the concentration of molecules that make a jump during dt toward $x+$, multiplied by their velocity: $v_{x+} = a/\mathrm{d}t$. We then obtain the total flux in mean-field theory

$$J = \{p_1C_S[k(1, 0)p_0 + k(1, 1)p_1] + 2p_2C_S[k(2, 0)p_0 + k(2, 1)p_1]\}a \qquad (A7)$$

Substituting the α and β dependence of $k(i, j)$ gives

$$J = k_0C_Sa(p_1 + 2\alpha p_2)(p_0 + \beta p_1) \qquad (A8)$$

from which we obtain

$$D_x(c) = \frac{k_0C_S}{c}(p_1 + 2\alpha p_2)(p_0 + \beta p_1)a^2 \qquad (A9)$$

We can write eq A9 using the more usual coverage dependence $\theta = c/c_{\max} = c/(2C_S)$ (since the sites can be doubly occupied)

$$D_x(\theta) = \frac{k_0}{2\theta}(p_1 + 2\alpha p_2)(p_0 + \beta p_1)a^2 \qquad (A10)$$

Note that if we suppose that the sites can only be singly occupied, then $\alpha = \beta = 0$. In this case, eq A10 reverts to the usual mean-field expression for the singly-occupied square lattice: $D_x(\theta_1) = D_x(\theta_1 = 0)(1 - \theta_1)$, where θ_1 is the fractional coverage on a lattice of singly occupiable sites.

Now p_0, p_1, and p_2 are completely defined by the following set of equations

(1) Conservation of the number of sites:

$$p_0 + p_1 + p_2 = 1 \qquad (A11)$$

(2) Conservation of the number of molecules:

$$C_S(p_1 + 2p_2) = c \Rightarrow p_1 + 2p_2 = 2\theta \qquad (A12)$$

(3) Detailed balance:

$$\frac{\partial p_0}{\partial t} = 0$$

$$= -p_04[p_1k(1, 0) + 2p_2k(2, 0)] + p_14[p_0k(1, 0) + p_1k(1, 1)]$$

$$0 = -2\alpha p_0p_2 + \beta p_1^2 \qquad (A13)$$

So that

$$p_0 = \frac{\alpha(2\theta - 1) + 4\beta(1 - \theta) - \sqrt{\alpha^2(2\theta - 1)^2 + 8\alpha\beta\theta(1 - \theta)}}{2(2\beta - \alpha)} \qquad (A14)$$

$$p_1 = -2(p_0 + \theta - 1) \qquad (A15)$$

$$p_2 = p_0 + 2\theta - 1 \qquad (A16)$$

Equations A9 and A14−A16 were used to generate the curves presented in Figure 5. Note that eq A9 is a mean-field expression that ignores all correlation effects between particles and jumps,[43−45] which have been shown to be important when nearest-neighbor interactions are considered.[31] Indeed, our own Monte Carlo calculations of the diffusivity in this simple system have shown that correlation effects appear even for low concentrations; however, the general shape of the curves remains the same. Correlation effects in a very similar system (excluding "β" interactions but allowing for up to five molecules in the same site) have been shown by Czarnecki et al. to be smaller than in a similar "hard-core" system, where only single occupancies are allowed.[42] Therefore, since this system has been studied in order to provide a simple qualitative picture of the influence of the interaction parameters α and β, we found it adequate to ignore correlation effects.

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