Dynamic Monte-Carlo and mean-field study of the effect of strong adsorption sites on self-diffusion in zeolites

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Abstract

Self-diffusion in zeolites is studied using a simple mean-field theory and dynamic Monte-Carlo simulations of diffusion on a lattice model of the zeolite pore space. Our method is powerful, because of its simplicity, flexibility and ability to study the influence of various factors: the topology of the pore network, the fraction of strong adsorption sites, the relative strengths of weak and strong sites, the number of sites per zeolite cage, and the ratio of intracage to extracage hopping probabilities. Notwithstanding the simplicity of the modeling, our results confirm the qualitative trends observed in pulsed-field gradient NMR experiments, and are able to explain them. For ZSM-5, we also found a new possible type of functional dependency of the diffusivity on occupancy, with two inclination points.

Keywords: Zeolites; Monte-Carlo; Mean-field; Diffusion; Lattice model

1. Introduction

An understanding of the factors which influence diffusion in zeolites is necessary, as separations and catalytic processes using zeolites are often diffusion limited. Of particular interest is the dependency of the self-diffusivity \( \mathcal{D} \) on the molecular occupancy \( \theta \) for various pore network topologies, and different types and numbers of sites. The diversity of forms of \( \mathcal{D}(\theta) \) is nicely illustrated in Kärger and Pfeifer’s review (1987) of PFG NMR experiments, in which they distinguish five types of dependencies of diffusivity on occupancy: monotonically decreasing (type I), constant and then decreasing (type II), increasing up to a constant plateau (type III), increasing until a maximum and then decreasing (type IV), and a quasi-parabolic increase (type V). These curves are also reproduced with experimental data in Figure 7.2 of Kärger and Ruthven’s book (1992). Kärger, Pfeifer and Ruthven offer an explanation for the shape of these functions, but mostly in qualitative terms.

Molecular simulations and theoretical models have helped to identify how zeolite pore size and connectivity, as well as adsorbate size and shape affect \( \mathcal{D}(\theta) \). Molecular dynamics, transition-state theory, mean-field theories and Monte-Carlo techniques have all been used to this end. An overview of these methods is beyond the scope of this paper (see, for example, Kärger and Ruthven, 1992; Theodorou and Wei, 1983; Scogin, 1988; June et al., 1991; Snurr et al., 1994; Van Tassel et al., 1994; Keffer et al., 1996; Auerbach et al., 1995; Theodorou et al., 1996; Auerbach, 1997).

Dynamic Monte-Carlo simulations on a lattice representation of the zeolite pore network are a particularly useful approach to study self-diffusion on time scales longer than those currently accessible by molecular dynamics. In such models, the zeolite pore network is represented by a lattice, on which molecules can hop from one coarse-grained adsorption site to another. This activated hopping mechanism is representative for most situations of diffusion of small molecules through zeolites. Although this approach has been used extensively, following the work of Theodorou and Wei (1983) for a two-dimensional square lattice, much less attention has been paid to the situation where the lattice is more complex and contains more than one type of site (Coppens et al., 1998, and references therein). Van Tassel et al. (1994) and Keffer et al. (1996) have used a Monte-Carlo lattice...
diffusion method with multiple sites per cage, but these authors only studied two particular systems: zeolite A or Y with \( q = 6 \) equivalent sites in cages, which are connected in a cubic or tetrahedral network. In their work, bonds may be permanently blocked by strongly adsorbed species or cations. Auerbach, Jousse and co-workers focused mainly on benzene in NaY and NaX (Auerbach et al., 1995; Auerbach, 1997; Saravanan and Auerbach, 1997; Jousse et al., 1998), and recently investigated trans-2-butene diffusion in silicalite-2 (Jousse et al., 1998). We study the dependency of diffusion on loading for a much wider range of possibilities, and discuss the examples of ZSM-5 and a cubic lattice.

The aim of our work was to investigate \( \mathcal{D}(\theta) \) for pore networks characteristic of a cubic lattice and ZSM-5, although our study can easily be extended to include other topologies. In addition to adsorbate occupancy, \( \theta \), we have examined the effects of the fraction of strong adsorption sites, \( f \); the ratio of the average adsorption times on strong and weak sites, \( \tau_s/\tau_w \); the number of adsorption sites per channel intersection (i.e., cage), \( q \); and the ratio of intracage to extracage hopping probabilities, \( \gamma \). Exact expressions are derived for the self-diffusivity in the limit of very low occupancy (\( \theta \to 0 \)), \( \mathcal{D}_0 \). Dynamic Monte-Carlo simulations are then carried out to determine \( \mathcal{D}/\mathcal{D}_0 \) for fixed values of \( f \), \( \tau_s/\tau_w \), \( q \), and \( \gamma \). We also derive mean-field results for the diffusivity in a zeolite with weak and strong adsorption sites. These analytical values are exact for \( q \to \infty \) and serve as a reference for the Monte-Carlo simulation results.

2. Analytical results

2.1. Diffusivity at very low occupancy, \( \theta \to 0 \)

Consider a general simple (Bravais) lattice consisting of cages linked by channels, with each cage having \( Z \) neighboring cages. Within a cage, there are \( q \) adsorption sites. A fraction \( f \) of all sites is strong, and the average adsorption time on them is \( \tau_s \). The remaining fraction \( 1 - f \) of the sites is weak, and the average adsorption time on them is \( \tau_w \). In the limit of low molecular occupancy, \( \theta \to 0 \), the diffusing molecules do not interact, so that the time spent on average on a site is

\[
\tau = f \tau_s + (1 - f) \tau_w.
\]

If all the sites were weak, the average adsorption time would be \( \tau_w \) and the diffusivity in this case is denoted by \( \mathcal{D}_0 \). When there are strong adsorption sites, the diffusivity is reduced by an amount equal to \( \tau/\tau_w \), so that

\[
\mathcal{D}_0 = \lim_{\theta \to 0} \mathcal{D} = \frac{1}{1 + (\tau_s/\tau_w - 1) f} \mathcal{D}_0.
\]

This relationship holds for any number of sites per cage.

The ratio of the diffusivity when there are \( q \) sites per cage to the diffusivity when there is only 1 site per cage is also readily calculated for the limit of low occupancy. Each site is surrounded by \( (q - 1) \) sites within the same cage, and \( qZ \) sites in neighboring cages. The probability for a molecule to attempt an intracage hop, i.e., a hop to any other site within the same cage, is \( p_c \), and the probability to leave the cage to any extracage neighbor is \( p_e \). These can differ in a practical situation (Van Tassel et al., 1994). Clearly,

\[
(q - 1)p_c + qZp_e = 1.
\]

By specifying \( \gamma = p_i/p_e \), the extracage hopping probability is known:

\[
p_e = \frac{1}{\gamma(q - 1) + qZ}.
\]

The probability to leave a cage is \( qZp_e \), and it is easy to show that the average time spent in a cage is \( \tau/(qZp_e) \), so that

\[
\mathcal{D}_0(q) = qZp_e \mathcal{D}_0(q = 1) = \frac{qZ}{\gamma(q - 1) + qZ} \mathcal{D}_0(q = 1).
\]

The pore network of ZSM-5 is not a Bravais lattice. It consists of pores connecting cages in which there are up to \( q \) adsorption sites. Each cage is connected to \( Z = 4 \) neighboring cages. The sites in these cages (called \( \beta \) sites) can be either strong or weak. However, in each pore channel, there is are also 1 site (called an \( \alpha \) site), which is always weak (Trout et al., 1997; Coppens et al., 1998). The unit cell of the ZSM-5 pore lattice is shown in Fig. 1. In a way analogous to the Bravais lattice, it can be shown that the average adsorption time in a cage is

\[
\tau_{\text{cage}} = \left[ \frac{\gamma(q - 1)}{4} + 1 \right] [f \tau_s + (1 - f) \tau_w].
\]

After leaving a cage, the molecule spends an average time \( \tau_w \) on an \( \alpha \) site, after which it again moves to a cage, and so on. Therefore, \( \tau = \frac{1}{2} \tau_{\text{cage}} + \frac{1}{2} \tau_w \) so that

\[
\mathcal{D}_0 = \lim_{\theta \to 0} \mathcal{D} = \frac{2}{[\gamma(q - 1)/4 + 1]} \left[ f \tau_s/\tau_w + (1 - f) \right] + 1 \mathcal{D}_0(q = 1).
\]

2.2. Diffusivity at arbitrary occupancy: mean-field theory

As explained in the introduction and in a previous paper (Coppens et al., 1998), for \( \theta > 0 \) a molecule has the
tendency to return to a site it has visited before, so that successive steps are correlated. Therefore, concentrations at various sites of the pore lattice are in general different and are mutually correlated, at least between nearest neighbors, but even further, as was shown for ZSM-5/silicalite (Coppens et al., 1998). Nevertheless, it is useful to calculate analytically a mean-field value for the diffusivity, because it enables us to quickly compare various situations in a qualitative way, and it is a basis for comparison with Monte-Carlo results. In passing, we will also derive formulas for the occupancies of strong and weak sites.

In a lattice with $s$ types of sites, the mean-field approximation consists in assuming that the occupancy of all sites of the same type $i$ is the same, $\theta_i$. For a Bravais lattice, $s = 2$: the occupancy of the strong sites is $\theta$, and the occupancy of the weak sites is $\theta_w$. For ZSM-5, $s = 3$, because we need to distinguish between $z$ sites (occupancy $\theta_z$) and strong and weak $\beta$ sites (occupancies $\theta_\beta$ and $\theta_{\beta w}$, respectively).

Suppose there are $n_i$ sites of type $i$ per unit cell ($n = \sum_i n_i$), and that a site of type $i$ has $Z_i$ neighbors, $Z_{ij}$ of which are of type $j$ ($\sum_j Z_{ij} = Z_i$). A molecule on a site of type $i$ attempts a hop each time $\tau_i$, on average, so that the attempted hopping frequency is $1/\tau_i$. The probability to hop to any site of type $j$ is $p_{ij}/(\sum_j p_{ij} = 1)$. If hops in every direction are equiprobable, $p_{ij} = Z_{ij}/Z_i$. However, it is reasonable to assume (see also Van Tassel et al., 1994) that the intracage hopping probability differs from the extracage hopping probability by a factor of $\gamma$. This does not have any effect on Bravais lattices, where the unit cell consists of a single cage, but it does for ZSM-5. The matrix $\{p_{ij}\}$ is given in the appendix.

Based on these definitions, we can derive equations for the occupancies and the diffusivity. The mass conservation equation states that

$$\sum_{i=1}^n n_i \theta_i = n \theta.$$

(9)

Under the mean-field approximation, the flow $F_{ij}$ from sites of type $i$ to sites of type $j$, per unit cell and per unit of time, is the product of the number of molecules on sites of type $i$ ($n_i \theta_i$), the attempted hopping frequency toward a site of type $j$ ($p_{ij}/\tau_i$), and the probability that the site of type $j$ is vacant $(1 - \theta_j)$:

$$F_{ij} = \frac{1}{\tau_i} n_i \theta_i p_{ij}(1 - \theta_j).$$

(10)

The flow from sites of type $i$ to sites of type $j$ should equal the reverse flow from sites of type $j$ to sites of type $i$, hence,

$$F_{ji} = F_{ij}.$$

(11)

If there are only two types of sites (weak and strong), Eq. (9) and the unique flow balance, Eq. (11), can be solved to yield $\theta$ and $\theta_w$ as a function of $\theta$ and $f(n_i = qf, n_w = q(1 - f), p_{sw} = 1 - f$ and $p_{ws} = f)$. For ZSM-5, 2 of the three flow balances (e.g., between $z$ sites and weak $\beta$ sites, and between $z$ sites and strong $\beta$ sites) are sufficient to solve for $\theta_z, \theta_\beta$, and $\theta_{\beta w}$, now as a function of $\theta, f$, and $\gamma$. The explicit calculations are straightforward, but a little cumbersome to write out, and the results are therefore provided in the appendix.

In Fig. 2, the occupancies of strong and weak sites in a cubic lattice, $\theta_\beta$ and $\theta_{\beta w}$, are shown as a function of the average occupancy $\theta$, for $\tau_z/\tau_w = 100$ and various values of the fraction of strong adsorption sites, $f$. Of course, for $f = 0$, $\theta_\beta = \theta$, and for $f = 1$, $\theta_\beta = \theta$. The strong sites are more quickly filled than the weak sites, especially when the fraction $f$ of strong sites is low. At relatively high occupancies and a low fraction of strong sites, almost all the strong sites are filled, because the residence time on the strong sites is much longer than on the weak sites. The curves for a lower ratio of adsorption times, $\tau_z/\tau_{\beta w}$, are similar, but closer to the diagonal.

Fig. 3 shows the occupancies of the three types of sites of ZSM-5 with 1 site per cage and 80% of strong cage sites ($f = 0.8$); in this figure, the probability for an attempted intracage hop is assumed to be much higher than for a hop to an $z$ site, out of a cage ($\gamma = 100$). It is clear from this figure that the different types of sites are titrated in succession: first the strong $\beta$ sites, as for the cubic lattice, then the weak $\beta$ sites, because they can be reached from the strong ones and $\gamma$ is high. The (weak) $z$ sites in the pore channels only start to be filled when the strong sites
and strong sites are similar to those for the cubic lattice. We will come back to this figure in connection with the plots for the diffusivity, as found from Monte-Carlo simulations.

A mean-field estimate for the diffusivity can be obtained by calculating the average time $\tau$ a molecule spends on a site and comparing this to the time $\tau_w$ spent on this site if all sites were weak and the occupancy close to zero. Then,

$$D = D_0 \frac{\tau_w}{\tau}. \quad (12)$$

At all times, a fraction $F_i/F$ of the total site-to-site flow $F$, where $F_i = \sum_j F_{iji}$ and $F = \sum_i F_i$, leads to sites of type $i$. The flows $F_{iji}$ are given by Eq. (10). If molecules stay an average time $t_i$ on a site of type $i$, the average time $\tau$ spent on any site is given by

$$\tau = \frac{\sum_i F_i}{F} t_i. \quad (13)$$

The average time spent on a site of type $i$ is easily verified to be

$$t_i = \frac{\tau_i}{\sum_j P_{ij}(1 - \theta_j)}, \quad (14)$$

so that all information to calculate the diffusivities is contained in the previously evaluated probabilities $\{P_{ij}\}$ and occupancies $\theta_i$, as given in the appendix for a cubic and a ZSM-5 lattice. For a Bravais lattice, Eq. (9) is used to prove that the last equation reduces to $t_i = \tau_i/(1 - \theta)$.

In Fig. 4a and b, normalized mean-field predictions of the diffusivity on a cubic lattice are shown as a function of the occupancy $\theta$, for $\tau_s/\tau_w = 10$ and 100, respectively. The results were normalized with respect to the analytically calculated value for the diffusivity at zero occupancy, $D_0$. Already with this simple model, we see familiar trends. First, a monotonic decrease with occupancy for very low or high fractions of strong adsorption sites (the latter is obvious, since $D_\theta = D_0 \tau_w/\tau_\theta$). Then, for intermediate values of $f$, a maximum, as observed by Kärg and Pfeifer (1987). This maximum is explained as

![Fig. 2. Occupancies of strong (---) and weak (-----) adsorption sites in a cubic network, as a function of the total loading $\theta$ for $\tau_s/\tau_w = 100$ and $f = 0.2, 0.5$ and 0.8.](image)

![Fig. 3. Occupancies of the strong $\beta$ and the weak $\beta$ and $\alpha$ adsorption sites in ZSM-5, as a function of the total loading $\theta$ for a fraction $f = 0.8$ of strong sites in the cages, $\tau_s/\tau_w = 100$, and $\gamma = 100$.](image)

![Fig. 4. Mean-field prediction of the self-diffusivity on a cubic lattice with 1 site per cage. (a) $\tau_s/\tau_w = 10$; (b) $\tau_s/\tau_w = 100$. In this and subsequent graphs, diffusivities are normalized with respect to the diffusivity at very low loading, $D_0 = D(0)$.](image)
follows. Strong adsorption sites are filled first (Fig. 2), especially at high ratios of average adsorption times $\tau_s/\tau_w$. Other molecules are now able to move more freely by hopping between mostly weak adsorption sites, leading to an increase in diffusivity, when compared to the diffusivity at very low occupancy. A maximum is reached, because at higher occupancies mutual obstruction becomes predominant: strong adsorption sites are almost fully occupied and weak adsorption sites start to be filled, thus hindering the movement of other molecules which attempt to leave a site. For low $f$, the maximum is reached earlier, because full titration of the strong sites is reached at a lower $\theta$ (Fig. 2).

It is important to note at this point that we cannot observe cases in which the diffusivity does not decrease to zero for $\theta = 1$, but instead reaches a plateau (type III) or monotonically increases (type V). Indeed, for a fully occupied lattice, no self-diffusion is possible under our assumption that diffusion occurs by hopping from site to site. In order to observe these other cases, we must assume that a filled cage or channel site does not completely block the cage or site. Such situations could be expected for small molecules or for larger molecules in large pore zeolites, situations where types III and V curves have been observed. Although relatively straightforward, we have not yet carried out simulations of this kind, which introduce more parameters. In this case, interactions between free and adsorbed molecules should probably be accounted for, making the model more complex.

From curves like those shown in Fig. 4a and b, we can reasonably expect that the mean-field results provide a qualitatively correct result, but we need Monte-Carlo simulations to obtain more quantitative results and to study the effect of the mentioned parameters in more detail.

### 3. Monte-Carlo simulations

Monte-Carlo simulations of diffusion on a lattice model of the zeolite pore network enable us to study more accurately the effect of geometrical parameters, such as the topology of the pore network, the fraction $f$ of strong adsorption sites and the number of sites per cage, $q$, and physico-chemical parameters, such as the relative strengths of strong and weak sites, $\tau_s/\tau_w$, and the ratio of intra-to-extracage hopping probabilities, $\gamma$.

As Bravais lattices are simpler than the ZSM-5 lattice, it is useful to first study self-diffusion on a cubic lattice, and then to investigate the similarities and differences with the more complex ZSM-5 lattice. Fig. 5a and b show the self-diffusivity on a cubic lattice with 1 site per cage for $\tau_s/\tau_w = 10$ and 100, i.e., these figures allow for direct comparison with the mean-field predictions in Fig. 4a and b. Although there are quantitative differences, the qualitative agreement is excellent, and even the correct mean-field prediction of a maximum for $f = 0.2$ is remarkable.

Fig. 6a shows the self-diffusivity on a cubic lattice for $f = 0.2$ and $\tau_s/\tau_w = 100$, for 1, 2 and 8 sites per cage. The dotted line shows the mean-field prediction, which is exact in the continuum approximation, i.e., for $q \to \infty$. The number of sites has a purely quantitative effect on the results: the maximum remains at around $\theta = 0.4$, but slightly rises due to an increased mobility when the connectivity of the sites is higher. The situation shown for $f = 0.8$ in Fig. 6b is somewhat different: although the diffusivity decreases in an almost linear way for low occupancy, a local maximum at high occupancy is predicted for lattices with a large number of sites per cage.

It should be noted that $\gamma$, the ratio of intra-to-extracage hopping probabilities, has no effect on the normalized results for a cubic lattice. The absolute values of the diffusivities will be lower, but the normalized curves for different values of $\gamma$ coincide, because $\gamma$ merely changes the average time spent by a molecule in a cage, and the whole diffusion process in the Bravais lattice can be seen as a movement between cages, instead of sites.

Quite similar results are found for ZSM-5 with 1 site per cage. Fig. 7a and b show the self-diffusivities for $\tau_s/\tau_w = 10$ and 100, respectively. Note that the normalized curves for silicalite ($f = 0$) and ZSM-5 with $f = 1$
do not coincide, because all $x$ sites are weak for all values of $f$; all the sites in the cages are strong for $f = 1$. The latter creates a situation with alternate strong and weak sites, because there is an $x$ site in between each pair of $\beta$ sites and vice versa, thus leading to additional negative correlations in the molecular motion, when compared with silicalite. In between these limits, again a maximum can be observed for not too high $f$, but now only if $\tau_s/\tau_w$ is sufficiently high. This is different from what was observed for the cubic lattice (Fig. 5). Indeed, already for silicalite, there are strong negative deviations from the almost linear mean-field result, due to the low connectivity of the ZSM-5 lattice (Coppens et al., 1998). When some of the sites are strong, these negative deviations are slightly compensated at low enough occupancies, by the creation of channels of vacant weak adsorption sites, again because the strong adsorption sites are filled first. This compensation is not enough to lead the diffusivity through a maximum, because the strong sites are all within cages, which have a connectivity of 4, as opposed to the $x$ sites, which have a lower connectivity of 2.

Not surprisingly, the addition of an extra site per cage ($q = 2$) in ZSM-5 leads to more pronounced maxima (Fig. 8). The highest peak remains around $f = 0.2$. Although not shown here, when $q \to \infty$, an analogous approach of the Monte-Carlo results to the mean-field predictions is found for ZSM-5 as for the cubic lattice.

However, the differences between lattices with different numbers of sites per cage are larger, because the connectivity of the $x$ sites ($2q$) differs from the connectivity of the $\beta$ sites ($q + 3$). The former becomes larger than the latter for $q > 3$. For a large number of sites per cage, the maximum increase in relative diffusivity, $\mathcal{D}/\mathcal{D}_0$, is found for $f > 0.2$.

Contrary to the cubic lattice, a simplification of the diffusion process to a movement between cages cannot be made, because of the presence of an $x$ site in each channel.
As a result, when there are several sites per cage, the ratio $\gamma$ of intra-to-extracage hopping probabilities starts to play an important role. Fig. 9a and b show the dependency of the diffusivity on loading for ZSM-5 with 2 sites per cage and $\tau_s/\tau_w = 100$, but a different fraction of strong adsorption sites: $f = 0.5$ in (a) and $f = 0.8$ in (b). When $\gamma$ increases, there is an enhanced back-and-forth movement between sites within a cage. For $f = 0.5$, this leads to an increased relative mobility, because strong and weak adsorption sites are alternately occupied, with, by definition, longer residence times on the strong sites. Therefore, the maximum in the diffusivity rises, and asymptotically reaches a constant at the dynamic equilibrium for a sufficiently high value of $\gamma$. For $f = 0.8$, however, an interesting new situation appears: the maximum for $\gamma = 0$ (no intracage mobility), shifts, for high $\gamma$, to a function with two inclination points and zero slope around the point of the maximum for $\gamma = 0$. Such a function has not been reported before, but is certainly plausible, and can be explained with the help of Fig. 3, which shows the occupancies of the different types of sites in this situation. As mentioned before, for $\gamma = 0$, $\theta_{\beta w} = \theta_s$, so the normal type IV function (with a maximum) appears. But for a high value of $\gamma$, strong $\beta$, weak $\beta$ and weak $\alpha$ sites are titrated in succession. The saturation point in the curve for $\theta_{\beta w}$, the starting point for the rise of $\theta_s$ and the inclination point in the titration curve for the weak $\beta$ sites nicely coincide with the zero slope in the graph for $D(\theta)$ in this situation. When strong adsorption sites are starting to be filled, at low occupancy, the diffusivity does not decrease so much. When also the weak sites start to be filled, more cages become blocked, but there is also less intracage movement from strong to weak sites, so a new plateau is reached. Finally, almost all the $\beta$ sites are filled, leading to more hindrance and another decrease in the diffusivity as $\alpha$ sites become occupied. Also notice that for $f = 0.8$, the back-and-forth movements within a cage do not increase the mobility in general as they do for $f = 0.5$, because there is mainly a movement from one strong to another strong adsorption site within a cage, so a cage remains blocked.

4. Conclusions

Analytical mean-field theory and simple Monte-Carlo simulations on a lattice model of the zeolite pore network are sufficient to recover the possible dependencies of the diffusivity on loading, $D(\theta)$, commonly observed in pulsed-field gradient experiments (Kärger and Pfeifer, 1987; Kärger and Ruthven, 1992). Our approach allows to understand the impact of different geometrical and physicochemical parameters on the long-time value of the diffusivity for the general situation of a sorbate diffusing in an arbitrary zeolite. Type I, II and IV dependencies (for which $D(\theta = 1) = 0$) were explicitly recovered, while type III and V ($D(\theta = 1) > 0$) could easily be predicted by extending our model to include the possibility of a nonzero molecular transmission through pore channels and cages in which all sites are occupied.

Despite its approximations (Coppens et al., 1998), the mean-field theory predicts the qualitative trends seen in the corresponding MC simulations remarkably well, except for poorly connected pore networks with a low number of sites per cage. The presence and location of a maximum in $D(\theta)$ can be predicted by mean-field theory, although the value obtained by this approach is too high, because correlations in the molecular motions are neglected. For ZSM-5 with a high Al/Si-ratio and multiple sites per cage, our simulations predict a new type of function, with two inclination points, if the ratio of intra-to-extracage hopping probabilities is high.

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### Notation

- $D$: self-diffusivity, m$^2$/s
- $D_0$: diffusivity close to zero occupancy, m$^2$/s
- $D_{00}$: diffusivity close to zero occupancy for $f = 0$, m$^2$/s
- $f$: fraction of strong adsorption sites in the cages ($0 \leq f \leq 1$)
- $F$: total flow to strong and weak sites, 1/s
- $F_{ij}$: flow from sites of type $i$ to sites of type $j$, 1/s
- $F_{s}$, $F_{w}$: flow to strong, resp. weak, adsorption sites, 1/s
- $n_i$: number of sites of type $i$
- $p_e$: extracage hopping probability
- $p_i$: intracage hopping probability
- $p_{ij}$: probability to hop from a site of type $i$ to one of type $j$
- $q$: number of sites per cage
- $s$: number of different types of sites in the lattice
- $t$: time, s
- $t_i$: average time spent on a site of type $i$, s
- $t_s$: average time spent on a strong site, s
- $t_w$: average time spent on a weak site, s
- $Z$: connectivity

### Greek letters

- $\gamma$: ratio between the intra- and extracage hopping probabilities
- $\theta$: molecular occupancy, loading ($0 \leq \theta \leq 1$)
- $\theta_q$: occupancy of strong adsorption sites
- $\theta_w$: occupancy of weak adsorption sites
- $\tau$: average time between hopping attempts, s
- $\tau_{cage}$: average adsorption time in a cage, s
- $\tau_i$: average adsorption time on a site of $i$, s
- $\tau_s$: average adsorption time on a strong site, s
- $\tau_w$: average adsorption time on a weak site, s

### Subscripts

- $i$: associated to sites of type $i$
- $s$: associated to strong sites
- $w$: associated to weak sites

### Appendix. Mean-field results for the occupancies and diffusivity

In this appendix, some intermediate results are given, which are used to calculate the occupancies and diffusivity in a Bravais lattice and in ZSM-5 with the mean-field approach outlined in Section 2.2.

In a Bravais lattice, such as the cubic lattice, there are $s = 2$ types of sites: strong and weak sites, with occupancies $\theta_q$ and $\theta_w$, respectively. Suppose there are $q$ sites per cage and a fraction $f$ of all sites is strong. The average number of strong sites per cage is $n_s = f q$; the average number of weak sites per cage is $n_w = (1 - f) q$. Eq. (9) reduces to

$$f \theta_q + (1 - f) \theta_w = \bar{\theta}.$$  \hspace{1cm} (A.1)

The probabilities $\{p_{ij}\}$ are: $p_{ss} = p_{ws} = f$ and $p_{ww} = p_{ws} = 1 - f$, independent of $\gamma$. Therefore, using Eq. (10), the flows are

$$F_{ss} = f^2 q \theta_q (1 - \theta_s)/\tau_s$$
$$F_{sw} = f(1 - f) q \theta_q (1 - \theta_w)/\tau_s$$
$$F_{ws} = f(1 - f) q \theta_w (1 - \theta_s)/\tau_w$$
$$F_{ww} = (1 - f)^2 q \theta_w (1 - \theta_w)/\tau_w.$$ \hspace{1cm} (A.2)

The flow balance, Eq. (11), reduces to

$$\theta_s (1 - \theta_w) = \frac{\tau_s}{\tau_w} \theta_w (1 - \theta_s).$$ \hspace{1cm} (A.3)

Elimination of $\theta_s$ between Eqs. (A.3) and Eq. (A.1) leads to a quadratic equation in $\theta_w$:

$$\left[ (1 - f) \left( \frac{\tau_s}{\tau_w} - 1 \right) \right] \theta_w^2 + \left[ \left( \frac{\tau_s}{\tau_w} \right) (1 - f) \right] \theta_w + \left( \frac{\tau_s}{\tau_w} - 1 \right) = 0,$$ \hspace{1cm} (A.4)

the solution of which depends on the fraction of strong adsorption sites, $f$, and the total occupancy, $\overline{\theta}$, only. The occupancy of the strong sites can now also be determined from, e.g., Eq. (A.1).

From Eq. (A.2), the flows $F_s = F_{ss} + F_{ws}$, $F_w = F_{sw} + F_{ww}$ and $F = F_s + F_w$ are calculated. The average adsorption time on strong and weak sites, $t_s$ and $t_w$, is given by Eq. (14), which, together with the previously calculated values for the probabilities $\{p_{ij}\}$ and Eq. (A.2), leads to the simple result given earlier: $t_s = \tau_s/(1 - \theta)$ and $t_w = \tau_w/(1 - \theta)$. These results are substituted into Eqs. (12) and (13) to yield the final mean-field expression for the diffusivity:

$$D = \frac{[1 + f(\tau_s/\tau_w - 1)](1 - \theta)^2}{f(1 - \theta)(\tau_s/\tau_w - 1) + (1 - \theta)} \hspace{1cm} (A.5)$$

which is independent of $q$. Eq. (2) was used to calculate the relation between $D_q$ and $D_{0q}$. For ZSM-5, the calculations are more complex, because there are three types of sites in a larger unit cell, with different connectivities for the $\alpha$ and the $\beta$ sites. However, the general formulas given in the text remain
valid. The parameters needed to calculate \( \theta_s \), \( \theta_p \), and \( \theta_{pw} \) have the following values. The number of sites: \( n_s = 4 \), \( n_{p_s} = 2q(1 - f) \), \( n_{p_w} = 2qf \), giving a total of \( n = 2q + 4 \) sites. The probabilities to move from one type of site to another can be written as a function of \( p_e \), the probability to move from a weak or strong \( \beta \) site to an \( \alpha \) site, i.e., out of the cage

\[
p_e = \frac{4}{\gamma(q - 1) + 4}.
\]  

(A.6)

With this value of \( p \)

\[
p_{s\alpha} = 0, \quad p_{a\beta} = 1 - f, \quad p_{s\beta} = f,
\]

\[
p_{b\alpha} = \frac{p_e}{1 + (1 - p_e)(1 - f)}, \quad p_{b\beta} = (1 - p_e)(1 - f), \quad p_{b\alpha} = (1 - p_e)f.
\]

(A.7)

The flows in Eq. (10) can now again be calculated explicitly as a function of the occupancies and the parameters \( (f, \tau_s, \tau_w, q, \gamma) \). Flow balances between the sites, Eq. (11), can be solved together with the mass balance, Eq. (9), to yield the following cubic equation for \( \theta_s \):

\[
\frac{4q(\tau_s/\tau_w)\theta_s}{q\theta_e + [2\tau_s/\tau_w - q\theta_e]\theta_s} + \frac{4q\theta_e(1 - f)\theta_s}{q\theta_e + (2 - q\theta_e)\theta_s} + 4\theta_s = (2q + 4)\theta.
\]

(A.8)

Note that the equation becomes quadratic for \( q = 1 \) or \( 2 \) and \( \gamma = 0 \) \( (p_e = 1) \). The occupancies of the strong and weak \( \beta \) sites are found to be

\[
\theta_{p\beta} = \frac{2(\tau_s/\tau_w)\theta_s}{q\theta_e + [2(\tau_s/\tau_w) - q\theta_e]\theta_s},
\]

(A.9)

and

\[
\theta_{p\omega} = \frac{2\theta_s}{q\theta_e + (2 - q\theta_e)\theta_s}.
\]

(A.10)

All the necessary information is now available to calculate the diffusivity from Eq. (12) (normalized using Eqs. (5) and (8)), by substituting the flows and the average times spent on sites, Eq. (14), into Eq. (13).

References


