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Monte Carlo simulations of self- and transport-diffusivities of 2-methylhexane in silicalite

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We report kinetic Monte Carlo (KMC) simulations of self- and transport-diffusivities of 2-methylhexane (2MH) in silicalite. The hopping rates of 2MH along the straight and zig-zag channels were chosen based on the calculations of Smit (*Faraday Discuss*., 1997, **106**, 93). The self-diffusivity tensor was found to exhibit anisotropy and strongly dependent on the occupancy or loading. The degree of anisotropy of the self-diffusivity tensor decreases with loading, a hitherto unreported result. The loading dependence is shown to be due to correlation effects. Such correlation effects, do not however influence the behavior of the transport-diffusivity which exhibits a predictable Langmuirian dependence on loading.

Introduction

A quantitative understanding of the transport of adsorbed molecules in zeolitic materials is of vital importance for applications such as the kinetic separation of different alkane isomers.[1]

The flux of a single component through a zeolite matrix

$$\boldsymbol{J} = -\rho D_{\text{transport}} \boldsymbol{\nabla}\Theta = -\rho D_{\text{jump}} \Gamma \boldsymbol{\nabla}\Theta \quad (1)$$

is essentially determined by two terms: a thermodynamic (Γ) and a kinetic (D_{jump}) quantity.[2] Here, Γ is the so called *thermodynamic* correction factor

$$\Gamma = \Theta \frac{\partial \ln p}{\partial \Theta}, \quad (2)$$

with Θ being the loading of the zeolite (molecules per unit cell) and p being the partial pressure of the adsorbed species. The jump-diffusivity D_{jump} reflects the kinetic microscopic particle mobility and is also referred to as the Maxwell–Stefan or "corrected" diffusivity.[3] ρ denotes the number of unit cells per volume. The product $D_{\text{jump}}\Gamma$ is also termed the *transport*-diffusivity.[2,3]

When the sorption isotherm exhibits a simple, single-site, Langmuir behavior the thermodynamic correction factor $\Gamma = 1/(1 - \Theta/\Theta_{\text{max}})$ and therefore Γ tends to infinity as saturation loading Θ_{max} is approached.[2,3] For some hydrocarbon molecules, such as branched alkanes and aromatics, the sorption is described by a dual-site Langmuir isotherm; in this case the thermodynamic correction factor exhibits a double maximum, again tending to infinity at saturation loading.[4] It is also clear from eqn. (1) that the flux across the zeolite $\boldsymbol{J}$ is also determined by the loading dependence of the Maxwell–Stefan diffusivity D_{jump}. Experimental data[2] show that for some solute–zeolite combinations D_{jump} is independent of the occupancy; in this case the product $D_{\text{jump}}\Gamma$ will have the same loading dependence as that of Γ.[4] However, experimental data for other molecule–zeolite combinations[2] show the Maxwell–Stefan diffusivity decreases with occupancy; in this case the loading dependence of the transport-diffusivity $D_{\text{transport}}$ will be more difficult to predict.

Even in simple systems, like the noninteracting lattice gas, the loading dependence of the self-diffusion coefficient is a function of the lattice topology, as has been recently shown by Coppens *et al.*[5] Moreover, for silicalite-like topologies, the loading dependence is strongly non-linear. So, to elucidate the particular behavior of diffusion in silicalite-type zeolites under high loading conditions, simulations with a clearly justified molecular picture are required.

The objective of the present contribution is to examine the loading dependence of the self-, jump-, and transport-diffusivities for a particular molecule–zeolite combination using kinetic Monte Carlo (KMC) simulation techniques. We have chosen the 2-methylhexane–silicalite system for two reasons. (1) It allows us to employ a well justified hopping model recently proposed by Smit *et al.*[6] (2) The system and model exhibit clearly Langmuir behavior and therefore the loading dependence of Γ is exactly known. In contrast to previous studies,[5,7,8] we take the effect of unequal transition probabilities for straight and zig-zag channels into account.

Moreover, we report a loading dependence of the anisotropy of the self-diffusivity tensor in silicalite, which is shown to be typical for the case of unequal transition probabilities. In order to elucidate this behavior more clearly, we report simulations where transition probabilities are systematically varied and compare them with the much simpler case of a two-dimensional square lattice.

Simulation method

We perform kinetic Monte Carlo (KMC) simulations of a Langmuir type system, which means that we have a lattice of equal sites which can be occupied by only one molecule at a time and there are no further molecule–molecule interactions. Particles can move from one site to a neighboring site *via* hops. The probability per unit time to move from one site to another is determined by transition rates k_{zz} and k_{str} for zig-zag (zz) and straight (str) channels (see Fig. 1 for a schematic sketch). This approach is furnished by recent configurational bias Monte Carlo (CBMC) simulations of Vlugt *et al.*[9] which reveal a clear Langmuir behavior for 2-methylhexane with a saturation limit of four molecules per unit cell. The Langmuir adsorption sites are found to correspond directly to the four channel intersections. In an earlier study Smit *et al.*[6] proposed a model for the diffusion of 2-methylhexane in silicalite at 300 K following the results also

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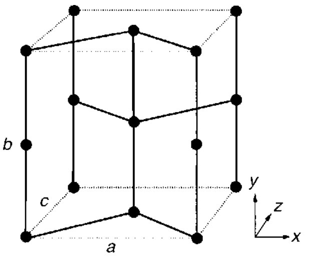

Fig. 1 Diffusion unit cell connecting intersection sites (black dots) *via* straight (str) and zig-zag (zz) channels (unit cell parameters: $a = 2.01$, $b = 1.99$, $c = 1.34$ nm).

obtained from a series of CBMC simulations using transition state theory[10] to determine the rate constants. From the simulations cited above it became quite evident that the bulky (branched) head group of the molecules prefers to stay in the intersections of the silicalite channel structure. Moreover, the preferred locations are separated by rather high free energy barriers of about 20 k_BT. Therefore, the average residence time (at ≈300 K) in an intersection is in the order of microseconds and thus diffusion in the zeolite structure might be described reasonably well by a model of uncorrelated jumps, as provided by the KMC/Langmuir approach.

We employ a standard KMC methodology to propagate the system (see refs. 11–13). A hop is made every KMC step and the system clock is updated with variable time steps. For a given configuration of random walkers on the silicalite lattice a process list containing all possible M moves to vacant intersection sites is created. Each possible move i is associated with a transition probability k_i, which is either k_{zz} or k_{str}. Now, the *mean* elapsed time τ is the inverse of the *total* rate coefficient

$$\tau^{-1} = k_{total} = \sum_{i=1}^{M} k_i, \tag{3}$$

which is determined as the sum over all processes contained in the process list. The actual KMC time step Δt for a given configuration is randomly chosen from a Poisson distribution

$$\Delta t = -\ln(u)k_{total}^{-1}, \tag{4}$$

where $u \in [0, 1]$ is a uniform random deviate. The timestep Δt is independent from the chosen hopping process. To select the actual jump, we define process probabilities according to $p_i = \sum_{j=1}^{i} k_j/k_{total}$. The ith process is chosen, when $p_{i-1} < v \leqslant p_i$, where $v \in [0, 1]$ is another uniform random deviate. After having performed a hop, the process list is updated. In order to sample ensemble averages correctly and to calculate dynamical properties more easily, the variable time scale is mapped on a periodic time scale for analyzing purposes. In order to avoid surface effects we employ periodic boundary conditions. We have investigated the finite size-effect on diffusivity and found convergence already at 5 × 5 × 5 unit cells. The employed rate constants, which should correspond to 2-methylhexane in silicalite at 300 K were $k_{str} = 1.4 \times 10^5$ s^{-1} for crossing straight channels and $k_{zz} = 5 \times 10^4$ s^{-1} for crossing zig-zag channels.[6]

Self diffusion and correlation effects

The self-diffusivity tensor may be described by components of the self-diffusion coefficient in the x-, y- and z-direction which are defined as

$$D_\alpha = \lim_{\Delta t \to \infty} D_\alpha(\Delta t) = \frac{1}{2} \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \langle r_\alpha^2(\Delta t) \rangle, \tag{5}$$

with $\langle \cdots \rangle$ denoting both ensemble and time averaging, where r is the particle displacement vector and α is x or y or z. Accordingly, the total self-diffusion coefficient is expressed by

$$D = \tfrac{1}{3}(D_x + D_y + D_z). \tag{6}$$

For uncorrelated hopping in silicalite type network structures Kärger[14] has established a relationship between the components of the diffusivity tensor

$$\frac{c^2}{D_z} = \frac{a^2}{D_x} + \frac{b^2}{D_y}, \tag{7}$$

where a, b and c are the dimensions of the rectangular unit cell in x-, y- and z-direction, respectively.

The self-diffusion coefficient of 2-methylhexane in a silicalite-type network structure at zero loading can be derived analytically and are given by Smit *et al.*[6]

$$\begin{aligned} D_x &= \tfrac{1}{4} k_{zz} a^2 \\ D_y &= \tfrac{1}{4} k_{str} b^2 \\ D_z &= \frac{1}{4} \frac{k_{str} k_{zz}}{k_{str} + k_{zz}} c^2. \end{aligned} \tag{8}$$

In Table 1 the values according to eqn. (8) and those obtained from KMC simulations are shown. Theoretical and simulated values agree well within the simulation uncertainty. The errors were determined using standard block averaging techniques.[15]

Fig. 2 shows the diffusion coefficients $D_\alpha(\Delta t)$ as a function of the time interval Δt. For D_x and D_y no significant time dependence can be denoted. For D_z, however, the situation is different. This has to be attributed to the fact that two processes (crossing straight and zig-zag channels) contribute to the diffusion in the z-direction. At long times the obtained diffusion coefficient corresponds to the value according to eqn. (8). At very short time intervals, only the crossing of a zig-zag channel contributes to the mean square displacement, since the combination of several jumps including movements along the straight channels is very unlikely. Hence, diffusion in the z-direction is not slowed down by straight channel moves. Consequently, the short time-limit for $D_z(\Delta t)$ can be expressed as

$$D_z(\Delta t \to 0) = \tfrac{1}{4} k_{zz} c^2. \tag{9}$$

This corresponds exactly to the case that Kärger has established for a completely correlated motion within the zig-zag channels.[14] The timescale separating these two general types of behavior is found to be in the range of the average residence time $\tau_R = 1/(2k_{str} + 2k_{zz}) = 2.63 \times 10^{-6}$ s.

In Fig. 2(b) the diffusion coefficient is shown for the occupancy of $\theta = 0.9$. Here, the fractional occupancy is defined as

Table 1 Self-diffusion coefficients for 2-methylhexane in a silicalite-like network structure at zero loading

	Diffusivity/10^{-14} m^2 s^{-1}			
	D	D_x	D_y	D_z
Eqn. (8)	6.854 78	5.050 14	13.860 36	1.653 84
KMC	6.848 ± 0.021	5.055 ± 0.018	13.836 ± 0.057	1.656 ± 0.006

The shown KMC simulation data correspond to a simulation run of 10^9 steps. The diffusion coefficients were obtained from particle displacements within a time interval of 10^{-3} s.

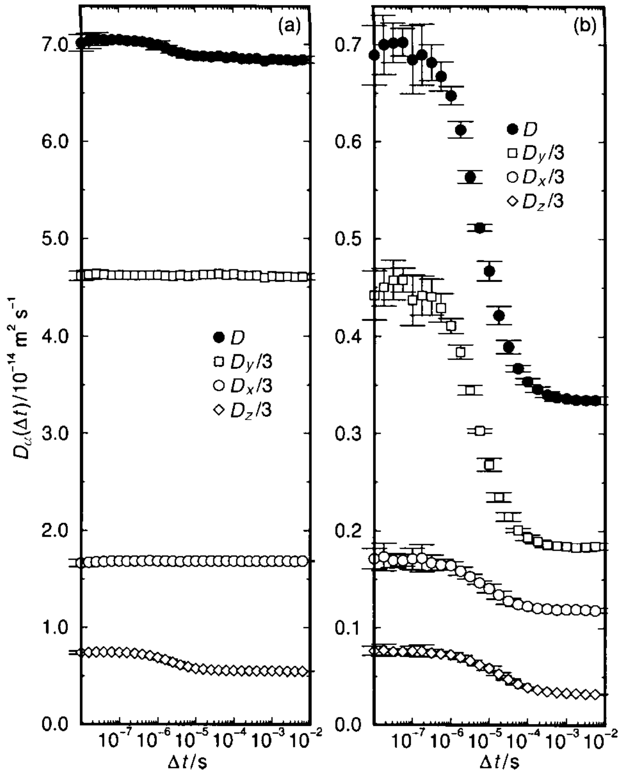

Fig. 2 Self-diffusion coefficients for 2-methylhexane in silicalite at "zero" loading (a) and at occupancy 0.9 (b) as a function of time. D_x, D_y and D_z denote the diffusivities in the x-, y- and z-direction, respectively.

$\theta = \Theta/\Theta_{\max}$, where $\Theta_{\max} = 4$ for the case under study. It is interesting to compare the short time limit of Fig. 2(a) and 2(b). The limiting values for $\theta = 0.9$ are exactly reduced by a factor of 10. The reason for this is illustrated in Fig. 3(a), where it is shown that the short time diffusion limit scales with $(1 - \theta)$. This is quite what is expected, since this is the probability for a particle to attempt a hop to a vacant neighboring site as already outlined by Coppens *et al.*[5] The long time limit, shown in Fig. 3(b), exhibits an additional slowing down of the self-diffusivity leading to a deviation from the ideal $(1 - \theta)$ behavior. This feature has to be attributed to a time dependent correlation effect, which depends (1) on the topology and is described quantitatively by the Kärger relation for the limit of zero occupancy and (2) on correlations due to the fact that a jump in the reverse direction is more likely, if the particle has performed a jump in a short time interval preceding that move.

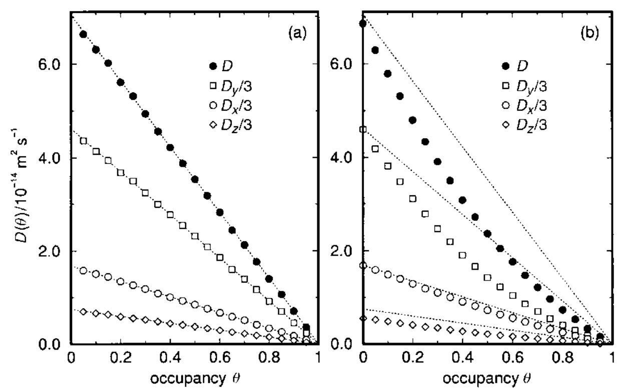

Fig. 3 Self-diffusion coefficients for 2-methylhexane in silicalite as a function of occupancy θ. D_x, D_y, D_z denote the diffusivities in the x-, y- and z-direction, respectively. (a) The short time limit ($D(\Delta t = 10^{-7}$ s)) scales exactly with $(1 - \theta)$. (b) The long time limit ($D(\Delta t = 10^{-3}$ s)) is additionally slowed down by particle time-correlations.

The strong correlation effect found here may indicate that the relation between average *scalar* connectivity and deviation from ideality as suggested by Coppens *et al.*[5] does not always hold. In the present case the connectivity is four, exactly corresponding to the value for a square lattice where the correlation effect is reported to be far less pronounced. Hence, the strong effect in silicalite is supposedly due to the peculiar connectivity of the silicalite channel structure, where the mobility in the z-direction is coupled to the mobility in the x- and y-direction.

A closer look at Fig. 2(b) reveals an interesting feature of diffusion on a silicalite lattice with unequal transition probabilities. While for the short time limit the difference between D_x and D_y is smaller than the difference between D_y and D_z the situation is *vice versa* for the limit of long times. This leads to the interesting conclusion that the anisotropy of self-diffusion is loading dependent. In order to illustrate this more clearly we have plotted the probabilities for a particle to move in the y- and in the x-direction

$$P_x^\theta = \frac{k_{zz}}{k_{zz} + k_{\mathrm{str}}} = \frac{D_z}{D_y}\frac{b^2}{c^2}$$

$$P_y^\theta = \frac{k_{\mathrm{str}}}{k_{zz} + k_{\mathrm{str}}} = \frac{D_z}{D_x}\frac{a^2}{c^2} \qquad (10)$$

as a function of loading in Fig. 4. Since the particle can only move either along a straight *or* a zig-zag channel, the probabilities to move in the x- and in the y-direction add up to unity, which is not subject to any correlation effect and therefore independent of loading (also indicating that the Kärger relation still holds at finite loading). However, as can be seen from Fig. 4, the individual weighting for these two processes *is* loading dependent. Moreover, the probability to make a move in the x- or in the y-direction is an apparently linear function of loading, indicating a less anisotropic diffusion tensor at high loadings.

To clarify this effect we have plotted in Fig. 5(a) the probability to make a move in the x- and in the y-direction at a loading close to maximum occupancy, P_x^1, P_y^1, as a function of the probability to make a move in the x-direction at zero occupancy P_x^0. In fact, P_x^0 is given by the fundamental transition probabilities k_{zz} and k_{str}, which were varied in a systematic manner and P_x^1 and P_y^1 were derived from diffusion coefficients obtained from simulations exhibiting only one unoccupied lattice site. The time between two sampled configurations was chosen in all cases large enough to yield converged diffusion coefficients. Again, for the considered P_x^0 parameter space, a system of 5 × 5 × 5 unit cells does not exhibit significant finite size effects.

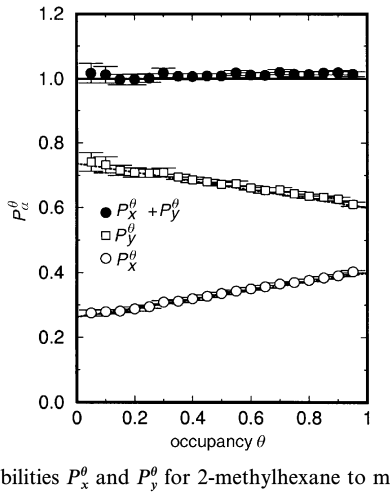

Fig. 4 Probabilities P_x^θ and P_y^θ for 2-methylhexane to move in the x- and y-direction, obtained from self-diffusion data according to eqn. (10).

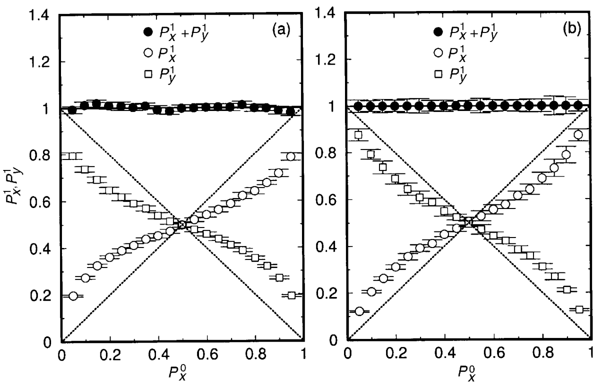

Fig. 5 Probabilities P_x^1 and P_y^1 for a particle to move in the x- and the y-direction in the high loading limit as a function of the transition probability at "zero" loading. Results for the silicalite lattice (a) and the square lattice (b). The dotted lines indicate ideal behavior in the absence of correlation effects.

First, the summed probabilities in Fig. 5(a) again suggest that the Kärger relation is fulfilled. We generally observe, that the correlation effects at high occupancy are always in opposition to the trend defined by the fundamental transition probabilities. For small probabilities to make a move in the x-direction, P_x^0, we find a preference to move in this direction at high loading, while for high probabilities, P_x^0 the opposite situation is found. For the case of equal transition probabilities ($P_x^0 = 1/2$) no loading preference can be observed.

The reason for this behavior can be demonstrated quite clearly by relating it to the much simpler case of diffusion on a square lattice with unequal transition probabilities in the x- and the y-direction (see also Fig. 5(b)). The correlation effect leads always to slowing down of the diffusion process, since it expresses nothing more than the possibility that a particle can make a move backwards (and therefore canceling the initial diffusion step). Obviously, this can happen only while the vacancy is still in the vicinity of a moving particle. Consequently, the correlation effect will be affected by any process influencing this jump-back probability. Let us consider now the two dimensional case. If the mobility in the x-direction is high, the probability to move in the y-direction will be small and therefore the high probability to reverse a diffusion step in the x-direction will result in a *large* correlation effect. Consider the opposite situation. Now the probability to move in the y-direction is high and therefore it is much more likely for the vacancy to make a move in the y-direction, reducing the probability to cancel the initial diffusion step in the x-direction. Consequently, the correlation effect in the x-direction will be *small*. A similar situation is found in the case of silicalite. Here, the correlation effect for a move along the straight channels will be large in the case of high straight channel transition probabilities.

It is interesting to note that from the molecular dynamics simulation results of Gergidis and Theodorou[16] a loading dependent diffusion anisotropy can also be conjectured. Their data (Fig. 16 of ref. 16) show a crossing of the average self-diffusion coefficient on n-butane in an n-butane–methane mixture and the diffusion in the x-direction at highest n-butane loadings, in accordance with the observation reported here.

Despite the fact that the observed loading dependence of the diffusion anisotropy is a rather weak effect, it is worth considering since it is a generic type of behavior for the case of unequal transition probabilities. Moreover, for a quite large number of alkane compounds the ratio of self-diffusivities in the x- and the y-direction at zero loading (which is equal to the ratio of fundamental transition probabilities) is close to the value observed for 2-methylhexane.[17] This has to be attributed to the fact that the transition probabilities are determined to a large extent by channel diameters given by the zeolite environment.

Jump- and transport-diffusivity

So far we have discussed self-diffusivities, denoting a quite complex direction dependent correlation behavior. The question arises, whether these effects influence mass transport *e.g.* through a silicalite membrane.

Due to the work of Reed and Ehrlich[11] and Uebing *et al.*[18,19] it is established that the thermodynamic correction factor Γ can be related to particle fluctuations in a finite probe volume

$$\Gamma = \frac{\langle N \rangle}{\langle N^2 \rangle} \tag{11}$$

at equilibrium conditions. Fig. 6(a) shows that the Γ-data obtained from KMC simulations approximate the expected $1/(1 - \theta)$ behavior for the Langmuir case rather well. For this purpose, the fluctuation of particles within one unit cell in a system of 5 × 5 × 5 unit cells has been considered.

To estimate the transport-diffusivity as an equilibrium property, a collective, so called "jump-diffusion" coefficient has been introduced[11,18]

$$D_{\text{jump}} = \frac{1}{6} \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \left\langle \left(\frac{1}{N} \sum_{i=1}^{N} r_i(t + \Delta t) - r_i(t) \right)^2 \right\rangle, \tag{12}$$

denoting the mean square displacement of the center of gravity of all N adsorbed particles. Since D_{jump} is identical with the Maxwell–Stefan diffusivity, the transport-diffusion coefficient $D_{\text{transport}}$ is the product of the thermodynamic factor (Γ) and D_{jump}. In Fig. 6(b) the different diffusion coefficients, are depicted as functions of the loading. Note, that D_{jump}, in contrast to D_{self}, is not subject to correlation effects and therefore shows exactly a $(1 - \theta)$ behavior. Since Γ and D_{jump} balance each other, the transport-diffusivity is estimated to be constant over the whole loading range. We would like to stress the fact that *self-* and *jump*-diffusivity are quantitatively different, which may serve as an additional reason for the disagreement between self-diffusion coefficients obtained from microscopic methods like neutron scattering and Maxwell–Stefan diffusivities according to flux measurements, as recently reported by Millot *et al.*[20] for isobutane. In general, however, for the case of two dimensional surface diffusion of interacting and noninteracting lattice gases both quantities typically exhibit a qualitatively similar loading dependence.[18,19]

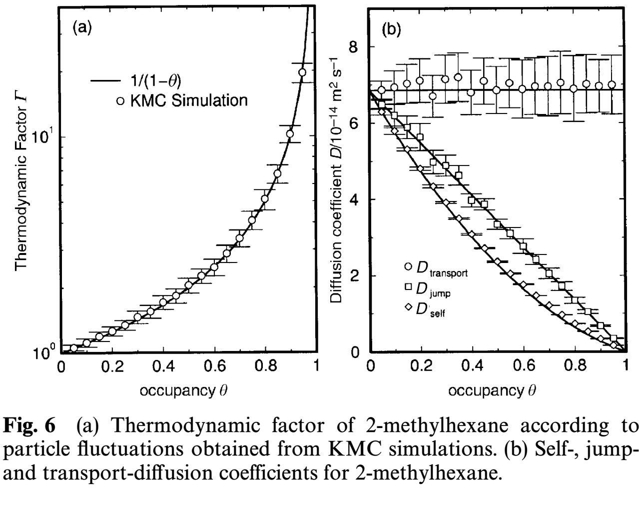

Fig. 6 (a) Thermodynamic factor of 2-methylhexane according to particle fluctuations obtained from KMC simulations. (b) Self-, jump- and transport-diffusion coefficients for 2-methylhexane.

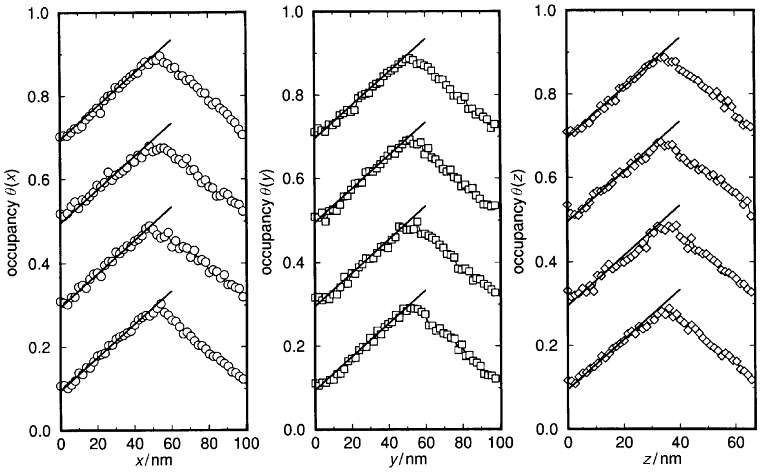

Fig. 7 Occupancy profiles obtained from nonequilibrium KMC simulations imposing fluxes in the x-, y- and z-direction. The time between subsequent particle transfers had been adjusted according to eqn. (13) ($\tau_x = 5.0 \times 10^{-5}$, $\tau_y = 1.8 \times 10^{-5}$, $\tau_z = 6.8 \times 10^{-5}$ s). The lines indicate the expected gradients.

Finally, we discuss the direct determination of transport-diffusivities from nonequilibrium KMC simulations. To simulate chemical transport directly, we have used a setup which differs from what was outlined above. In order to impose a precisely defined flux, we introduce two different regions within the periodic lattice: one region, from which randomly selected particles are taken out (source region), and one region, where particles are inserted at a randomly chosen site (target region). These transfer moves were done at a fixed rate, thus creating a constant particle flux. The resulting concentration gradient is a direct measure of the transport-diffusivity

$$D_{\text{transport},\,\alpha} = \frac{1}{4}\,\frac{n_\alpha}{n_\beta n_\gamma}\,\frac{b_\alpha^2}{\tau_\alpha}\,\frac{1}{\Theta_{\max}}\,(\Delta\theta)^{-1}. \qquad (13)$$

Here α specifies the direction of the particle transfer. $\Delta\theta$ is the difference in occupancy between target and source region, τ_α specifies the time between two particle transfers. n_α, n_β and n_γ give the number of unit cells and b_α specifies the length of one unit cell in the transfer direction.

For the nonequilibrium KMC simulations we have employed a simulation box, which was elongated in the transport direction by a factor of ten ($5 \times 5 \times 50$ unit cells). The regions (source and target regions) for particles to be transferred were chosen to be four unit cells thick. In very rare cases it happened that particle transfers at a certain time-step could not be executed since due to particle fluctuations either all target sites were blocked, or all source sites were empty. In order to maintain an overall constant flux, an additional particle has then been transferred at the subsequent transfer move. In Fig. 7 occupancy distributions obtained from nonequilibrium KMC simulations are shown. To build up gradients of comparable magnitude for different directions, the times between two particle transfers had been carefully adjusted (see caption of Fig. 7). In all cases, 10^7 simulation steps were sufficient to establish converged gradients, while another 3×10^7 were employed to sample configurations. About 10^3 configurations were stored at each run for analysis purposes. In accordance with the expectation of a loading independent transport-diffusivity, the obtained particle concentration profiles do not show any significant loading dependence and exhibit a well defined linear shape. Moreover, the obtained gradients match the transport-diffusivity value perfectly.

Conclusions

We have performed kinetic Monte Carlo (KMC) simulations of 2-methylhexane adsorbed in a silicalite type network structure. We have calculated direction dependent self- and transport-diffusivities. The self-diffusion exhibits a rather complex behavior based on the additional slowing down due to correlation effects, which have been reported previously. Since the mobility is direction dependent, the correlation effect is also direction dependent, resulting in a hitherto unreported decrease of the (self)-diffusivity anisotropy with increasing loading. This effect has been shown to be related to the presence of unequal transition probabilities for straight and zig-zag channels. It can also be found in the much simpler case of diffusion on a square lattice with unequal transition probabilities in the x- and the y-direction. Despite this rather complex scenario, the flux through a zeolite membrane is not affected by these correlation effects since the Maxwell–Stefan diffusivity has to be identified with the so called "jump-diffusion" coefficient of the center of mass motion of all adsorbed particles. The jump-diffusivity and the thermodynamic factor balance each other, leading to a loading independent transport diffusivity. This has been additionally shown by nonequilibrium KMC simulations, where a constant flux has been imposed and loading independent steady state gradients have been obtained.

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