RANDOM WALK TREATMENT OF DUMB-BELL MOLECULES IN AN LTA ZEOLITE AND IN CHABAZITE

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ABSTRACT

We analyse the mechanisms of self diffusion in zeolite-guest systems which show a non-monotonic temperature dependence of the self diffusion coefficient D: ethane in a cation-free LTA zeolite [1] and chlorine in silicious chabazite. In these systems D is influenced by jump rates for crossing energetic barriers as well as for crossing entropic barriers [1]. The entropy-controlled jump rates were found to *decrease* with increasing temperature. Employing random walk descriptions, simple analytical formulas are derived which relate the self diffusion coefficient of the guest molecules with the jump rates for crossing the different barriers. The simple ansatz we use can be transfered to other zeolite-guest systems.

INTRODUCTION

The diffusion of guest molecules in zeolites plays an important role in many industrial applications of various species of these porous materials as the time scale of practically all such applications is determined by diffusive processes. Zeolites are used as ion exchangers, molecular sieves and adsorbents. The applications include a wide variety of technical processes e.g. in the petrochemical industry, detergents and many others. By smart use of effects connected with the basic processes mentioned above zeolites can be used even in applications that seem to exclude each other such as car heating or cooling beer.

Two members of the zeolite family are the cubic Linde type A (LTA) zeolite and chabazite (CHA). Fig. 1 illustrates the shape of cages and the interconnectivity of the cages for these two zeolites. The left picture shows the cubic structure of LTA zeolites. The large α-cage has a free diameter of ≈ 1 nm

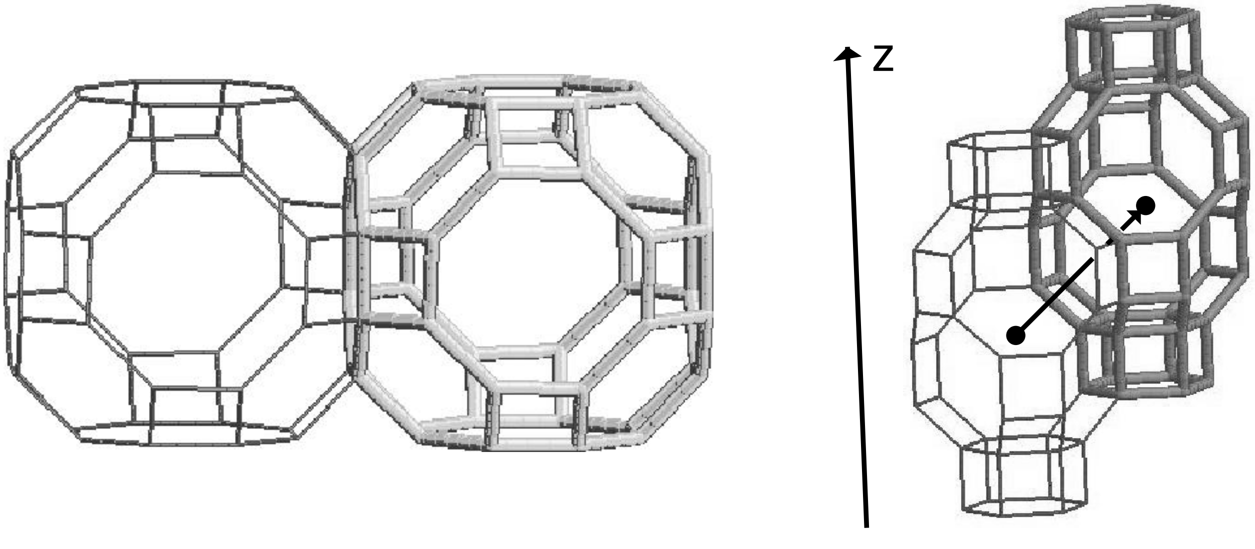

Figure 1: Structure scheme of LTA zeolites (left) and of chabazite. The vertices mark the positions of the T–atoms, the lines symbolize the oxygen bridges between them.

and the distance between the centers of adjacent cages is $L = 1.23$ nm. The 8–rings which are often called windows have a free diameter of ≈ 0.41 nm. They build the connection between the cages and can be passed by small hydrocarbons such as ethane. The structure of chabazite is more complicated as can be seen on the right hand site of Fig. 1. The picture shows two cages that are connected to each other by 8–rings. The distance between the centers of two such cages is 0.942 nm. In both zeolites the double 6–rings cannot be entered by the guest molecules which are considered in the present paper. The characteristics of interest here that the LTA and the CHA zeolite have in common are a spacious cage on the one hand and a narrow window between the cages on the other hand.

Earlier investigations of the dynamics and the diffusion of ethane in the cation free zeolite LTA showed a surprising temperature dependence of the self diffusion coefficient D. It turned out that this dependence is related to an entropic barrier [1] which is connected with the strong restriction for translation and rotation of the molecule in the small 8-ring compared to the spacious α-cage. In many cases the self diffusivity can be expressed as

$$D = \frac{1}{6} k L^2, \tag{1}$$

where k is a site-to-site rate constant and L is the cage-to-cage distance. By use of the transition state theory (TST) an expression for k can be derived.

$$k^{\mathrm{TST}} = \left[\frac{\omega(T)}{2\pi} \exp\left\{ \frac{\Delta S(T)}{k_{\mathrm{B}}} \right\} \right] \exp\left\{ -\beta \Delta E(T) \right\}. \tag{2}$$

$S(T)$ is the local entropy, $E(T)$ is the local total energy of diffusing particles, and k_{B} is the BOLTZMANN constant. The local entropy is obtained by $F = E - TS$ from the local free energy that is defined by the reversible work theorem [2]. Detailed examinations in [1] showed that the local entropy but not the local energy has a barrier at the window that connects adjacent cages in the zeolite. k was found to decrease with increasing temperature over a significant temperature range (150-300 K). We naively expected the temperature dependence of the self- diffusion coefficient, D, to follow that of k, but this was not observed in our molecular dynamics (MD) simulations. In what follows, we find that this discrepancy is caused by geometrical correlations, which we analyze below.

To understand the diffusion mechanism in detail we use a simple model which coarse-grains the particle trajectories to jumps between adsorption sites. A random walk treatment that has been derived in [3], basing on a method proposed in [4], is employed. If uncorrelated cage-to-cage jumps actually were to take place from cage-center to cage-center in the cubic arrangement of cages in the LTA zeolite, then Eq. (1) holds [5]. Uncorrelated jumps means that the probability of the direction of a move of a guest molecule through one of the six windows of a cage to an adjacent cage does not depend upon the direction of the preceding move. However, our MD simulations show that the naive expression in Eq. (1) overestimates the actual self diffusivity by nearly an *order of magnitude* at 100 K [3]. A correlation factor f can be defined by

$$f = \frac{D}{\frac{1}{6} k L^2} \qquad \text{hence} \qquad D = \frac{1}{6} k L^2 f, \tag{3}$$

where D is the self diffusion coefficient as obtained from Molecular Dynamics simulations via the EINSTEIN relation

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{\mathrm{d}}{\mathrm{d}t} \left\langle \left(\vec{r}(t) - \vec{r}(0) \right)^2 \right\rangle. \tag{4}$$

The more detailed investigation of the proposed random walk model in [3] and in the present paper yields analytical results for the correlation factor f.

A similar temperature dependence can be expected for other zeolite-guest systems for which some conditions are fulfilled. These conditions include a certain ratio of molecule size and window size on the one hand and a large zeolite cage on the other hand. Furthermore, restriction of rotation in the window increases the entropic barrier so that linear or dumbbell-shaped molecules like ethane are

interaction	σ / nm	ϵ / kJ/mol
CH_3–CH_3	0.378	0.866
CH_3–O	0.317	1.180
CH_3–Si	0.212	0.683
Cl–Cl	0.350	0.660
Cl–O	0.303	1.030
Cl–Si	0.198	0.596

Table 1: Lennard–Jones potential parameters for ethane and chlorine.

most likely to show the described effect. Therefore, the diffusion of ethane and chlorine has been investigated in a purely silicious zeolite of chabazite structure.

Because of the anisotropy of chabazite the diffusion tensor has to be considered where the components in xy–plane and in z–direction are different. The distances of the centers of adjacent cages are $r = 0.791$ nm in xy–direction and $h = 0.492$ nm in z–direction. Under the assumption of only a single cage-to-cage jump rate k simple formulas for uncorrelated diffusion similar to Eq. (1) are [5]

$$D_{xy} = \frac{1}{4}kr^2 \qquad D_z = \frac{1}{2}kh^2, \tag{5}$$

from which a relation

$$\frac{D_z}{D_{xy}} = \frac{2h^2}{r^2} = 0.78, \tag{6}$$

follows immediately. But, in NMR investigations of the diffusion of water in chabazite a ratio of 0.4 has been found [6]. The random walk model treatment proposed in the present paper yields a possible explanation for this discrepancy.

SIMULATION DETAILS

The MD simulations for ethane in the cation free LTA zeolite employed a cubic simulation box of a length of 2.46 nm containing 8 α-cages. The equilibirium coordinates of the oxygen- and the T-atoms were taken from [7] for zeolite LTA and from [8] for chabazite. In the case of chabazite the dimensions of the MD box were x_0=2.71 nm, y_0=2.34 nm, and z_0=2.95 nm. The volume of the simulation box which is compareable to the box for zeolite LTA contains 24 cages, i.e. the chabazite cages are considerably smaller than the α-cages of zeolite LTA. In both zeolites 8 guest molecules were included into the simulation box. The zeolite lattice flexibility was modeled according to [9, 10]. The Lennard-Jones interaction parameters were taken from [11] for CH_4-O and transfered to CH_3-O using the combination rules of Lorentz-Berthelot. The same has been done for CH_3–Si. From [12] the parameters for CH_3-CH_3 were obtained. The interaction parameters for the simulations with chlorine were taken from [13]. All Lennard-Jones interaction parameters are listed in Table 1. For the integration of the equations of motion the velocity-Verlet algorithm was used with a time step of $h = 1$ fs.

ANALYTICAL TREATMENT AND RESULTS

Jump rates and jump probabilities between adsorption sites can be taken from an MD run. Following [4] the series of all possible jump events are summed up and an expression for the diffusion coefficient can be derived analytically.

ETHANE IN CATION-FREE ZEOLITE LTA

First we examine diffusion of ethane in the simple cubic network of the α-cages of zeolite LTA. The jumps between the cages show correlations due to the additional sublattice of adsorption sites within the cage which is shown in Fig. 2. In analogy with the theory of vacancy diffusion [5] we employ a

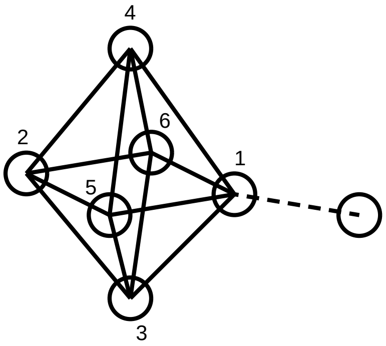

Figure 2: Schematic of the site connectivity for the jump model of ethane in LTA zeolite. The dotted line symbolizes the connection through the window to a site in an adjacent cage

correlation factor f

$$f = \frac{1 + \langle \cos\Theta \rangle}{1 - \langle \cos\Theta \rangle}, \tag{7}$$

where Θ is the angle between two successive cage-to-cage jumps, to include the influence of these correlations on D. Following the enumeration in Fig. 2 we let site 1 be the position where the molecule entered the cage. With the probabilities P_i that the molecule leaves the cage from site $i = \{1, ..., 6\}$ we obtain

$$\langle \cos\Theta \rangle = P_1 \cos 180^\circ + P_2 \cos 0^\circ = P_2 - P_1 \tag{8}$$

(the other possibilities do not contribute in the case of zeolite LTA due to $\cos 90^\circ = 0$). The problem is reduced to the derivation of the probabilities P_i which are connected to the jump rates occuring in the system. This simple ansatz can be transfered to other zeolite-guest systems for an analytical treatment of the diffusion.

Assuming now the molecule has just entered the cage and is at site 1, there are three possibilities for the following jump:

A leave the cage immediately,

B jump inside the cage to one of the sites 3…6 according to the connectivity in Fig. 2, or

C jump through the middle of the cage to site 2.

Let p_{ww} be the probability for possibility A, i.e. a jump through the window is followed by an immediate jump back, let p_{ws} be the probability for possibility B, i.e. a jump through the window is followed by a jump within the cage, and let p_{cr} be the probability for possibility C. p_{cr} is found to very low because the potential energy in the cage is ≈ 10 kJ/mol higher than at the zeolite walls. Thus, we neglect possibility C in the first approximation.

Due to the simple structure of LTA zeolite we only need the difference $P_2 - P_1$ to obtain $\langle \cos\Theta \rangle$ in Eq. 8. Now, if the molecule follows possibility B, it is found at one of the sites 3…6. From these positions, the sites 1 and 2 are reached with equal probability (!), i.e. these contributions to P_1 and P_2 vanish in the difference $P_2 - P_1$, thus

$$\langle \cos\Theta \rangle = -p_{\mathrm{ww}} \tag{9}$$

and

$$f = \frac{1 - p_{\mathrm{ww}}}{1 + p_{\mathrm{ww}}} \tag{10}$$

hold.

Extensive MD simulations on ethane in LTA over the temperature range of 80-1000 K yield excellent agreement between the correlation factor given in Eq. (3) and its approximation in Eq. (10). The

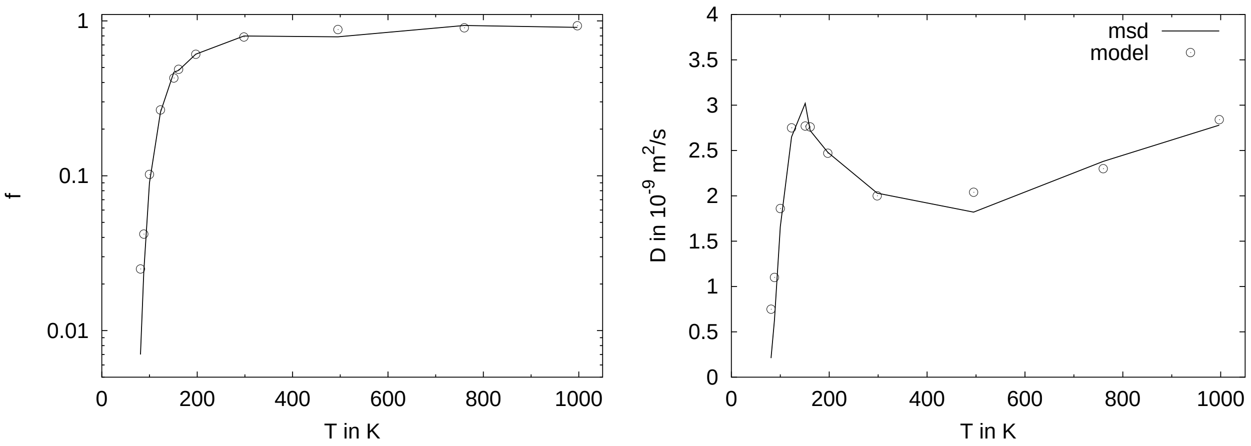

Figure 3: Left: Comparison of the correlation factors defined in Eq. (3) (line) and Eq. (10) (symbol). Right: Comparison of self-diffusion coefficients calculated from mean square displacements (msd) via the Einstein equation and from the jump model.

analytical expression for the self diffusion coefficient D resulting from the random walk model is checked by comparison with D values that are calculated directly from the trajectory by use of the Einstein relation. The inclusion of $p_{\rm cr}$ into the model increases the accuracy only slightly so that the simple expression Eq. (10) is a good approximation [3].

The strong correlations at low temperature result from the potential energy surface for the guest molecule ethane in the LTA zeolite. Local minima of the potential energy are situated in the centers of the windows. At low temperatures the molecules oscillate in the window and an energtic barrier in front of the window needs to be crossed to reach the other sites in the cage [3]. The narrow windows, however, are entropic barriers for the molecules [1]. The movement of the molecules happens at low temperatures mostly along the zeolite walls and the molecules easily find their way through the window. The probability to find molecules in the spacious cage increases strongly with increasing temperature while the probability to find the window passage decreases. In terms of the TST Eq. (2) this is equivalent with a decreasing jump rate k.

The jump rate $k_{\rm w}$ for crossing the window as well as the probability $p_{\rm ww}$ can easily be obtained from the evaluation of the MD trajectories of the molecules. The jump rate $k_{\rm ws}$ for escaping the potential minimum in the window is given implicitely by the relation

$$p_{\rm ww} = \frac{k_{\rm w}}{k_{\rm w} + k_{\rm ws}}. \tag{11}$$

For the self diffusion coefficient follows

$$D = \frac{L^2}{6} \left(\frac{1}{k_{\rm w}} + \frac{2}{k_{\rm ws}} \right)^{-1}. \tag{12}$$

Both jump rates $k_{\rm w}$ and $k_{\rm ws}$ are shown in Fig. 4 (left). While $k_{\rm ws}$ shows the usual Arrhenius type temperature depencence

$$k(T) = k_0 \exp\{-E_{\rm A}/k_{\rm B}T\} \tag{13}$$

with a positive activation energy of $E_{\rm A} = 1.7$ kJ/mol, $k_{\rm w}$ decreases with increasing temperature, the temperature coefficient $E_{\rm A} = -2.4$ kJ/mol is negative due to the entropic barrier [1]. The right side in Fig. 4 shows an Arrhenius plot of the self diffusion coefficient. Considering Eq. (12) it comes clear that always the lowest jump rates dominates D. This is the rate $k_{\rm w}$ at high and $k_{\rm ws}$ at low temperatures.

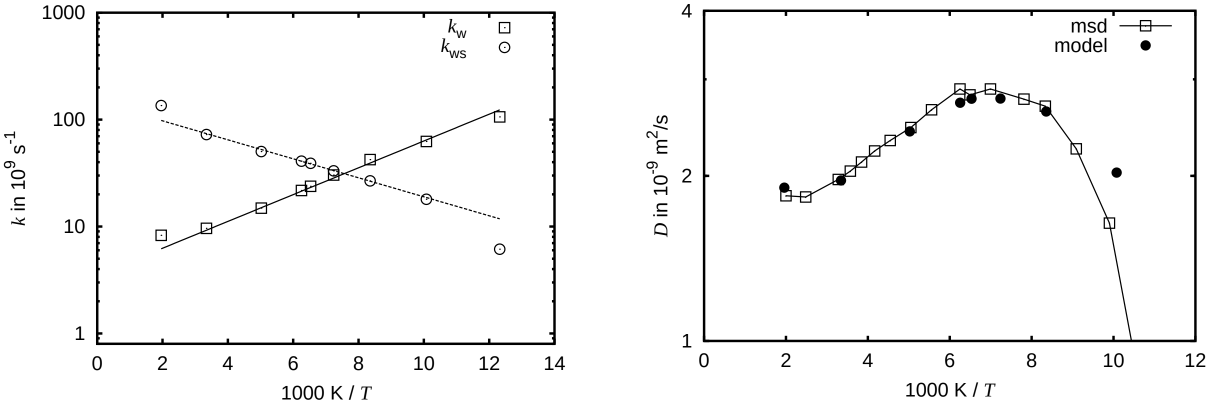

Figure 4: Left: Jump rates for crossing the energetic barrier in front of the window (k_{ws}) and the entropic barrier in the window (k_{w}). Right: ARRHENIUS plot of self-diffusion coefficients calculated from mean square displacements (msd) via the EINSTEIN equation and from the jump model.

ETHANE AND CHLORINE IN SILICIOUS CHABAZITE

Chabazite has, like zeolite LTA, cages which are connected by narrow 8-ring windows. Therefore, it is a candidate system where the effect of a non-monotonic temperature dependence of the self diffusion coefficient can occur and should be measurable in experiments. The 8-ring of chabazite (0.38 nm diameter), however, is slightly smaller than in zeolite LTA (0.41 nm). For this reason the simulations with the smaller chlorine molecule (compare Table 1) were supplemented to those with ethane.

The considered guest molecules ethane and chlorine adsorb on top and bottom of the chabazite cages (see Fig. 1). When a molecule passes the window it changes from e.g. a top position in the one cage to a bottom position in the adjacent cage. The resulting site topology is shown in Fig. 5. The diffusion in the xy-plane can be described as movement in parallel planes which can be changed by a jump within the cage. Due to this fact diffusion in z-direction is also possible.

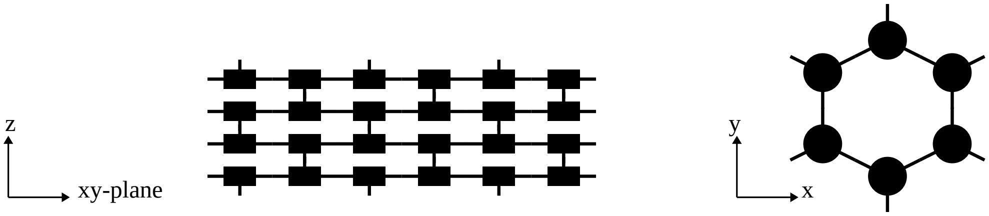

Figure 5: Schematic of the site topology in silicious chabazite.

The analytical treatment for the self diffusion of guest molecules in chabazite given in detail in [14] is straightforward for D_{xy} and leads to an expression analogous to Eq. (5)

$$D_{xy} = \frac{1}{4} k_{xy} r^2. \tag{14}$$

Here, the correlation factor f is equal to one when the three possibilities to jump in the xy-plane have the same probability. This was found to be the case indicating that the molecules relax at the sites.

The diffusion in z–direction needs more sophisticated considerations because each move of the guest molecule in z–direction in a cage ends at the cage walls where no outlet in z–direction exists. Therefore, moves larger than the cage size can be realized only by jumps in the xy-plane to adjacent cages. i.e. they need moves xy–direction. Cumbersome calculations in [14] yield

$$D_z = \frac{h^2}{2} \frac{k_z k_{xy}}{k_z + k_{xy}} = \frac{h^2}{2} \left(\frac{1}{k_z} + \frac{1}{k_{xy}} \right)^{-1}. \tag{15}$$

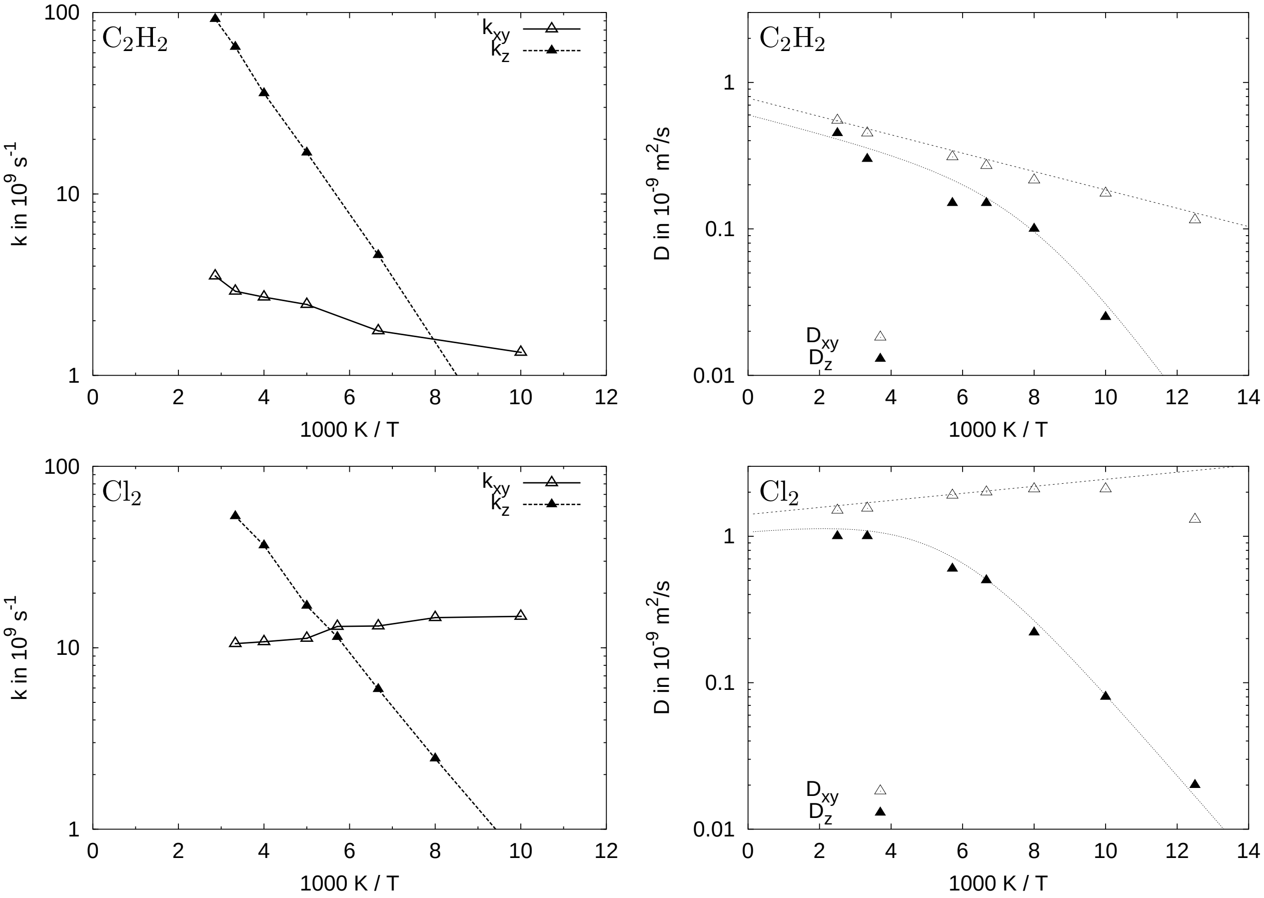

Figure 6: Comparison of the self-diffusion coefficients from MD simulations and analytical treatment for ethane and chlor in chabazite. The lines correspond to the analytical results while the symbols represent values obtained from the MD trajectories using the EINSTEIN relation.

This result is equivalent to the diffusion mechanism in the z-direction found in [15] for silicalite. When the channel crossings are considered as adsorption sites the site topology in the yz-plane of silicalite is exactly the same as in Fig. 5.

Instead of Eq. (6) the relation

$$\frac{D_z}{D_{xy}} = \frac{2h^2}{r^2}\frac{k_z}{k_z + k_{xy}} \tag{16}$$

between the components of the diffusion tensor follows immediately. The ratio D_z/D_{xy} depends on the temperature and approaches $2h^2/r^2$ for $k_z \gg k_{xy}$ i.e. when the barrier in the center of the chabazite cage vanishes or the barrier for crossing the window is high.

Fig. 6 shows the simulation results for ethane (top) and chlorine in silicious chabazite. The jump rates (left hand side of Fig. 6) k_{xy} and k_z have different temperature dependences. The rates k_z increase with increasing temperature with activation energies of ≈ 6 kJ/mol. The rates k_{xy} show a weak temperature dependence. In the case of ethane the activation energy is 1.2 kJ/mol and when fitting data for chlorine to the ARRHENIUS law a negative temperature coefficient of -0.4 kJ/mol results. This is in analogy to the result for ethane in cation-free zeolite LTA described above. However, the slope of the cage-to-cage rate is lower for chlorine in chabazite than for ethane in zeolite LTA. This can be explained by the smaller cage in the case of chabazite which leads to a smaller entropic effect.

The rigth hand side of Fig. 6 shows the diffusion coefficients of the considered guest molecules. The values calculated using the EINSTEIN relation are plotted as symbols. For comparison with the jump model, the ARRHENIUS fits for the jump rates are inserted into Eqs. (15) and (16) and the resulting curves shown as lines. The excellent agreement with the values for D from the EINSTEIN relation shows the validity of the jump model.

CONCLUSIONS

Employing a random walk model for the diffusion of ethane in an LTA zeolite and it could be shown how the interplay of two effects leads to the non-monotonic temperature dependence of the self diffusion coefficient D. This effect was also found for the diffusion of guest molecules in chabazite. Because the windows in chabazite are somewhat smaller than in the LTA zeolite the effect did not appear for ethane but for the slightly smaller chlorine molecule. The jump models for the diffusion in chabazite also showed the influence of different jump rates on D_z and the relation between the components of the diffusion tensor.

The results show that the effect of a non-monotonic temperature dependence of D occurs if the diffusion limiting jump rate decreases with increasing temperature. This decrease can occur when strong entropic effects are present, which result in the case of zeolite LTA and chabazite from the combination of a narrow window and spacious cage. The size of the molecule must not be larger than the size of the window (compare the results ethane and chlorine in chabazite) so that the window is no energetic barrier. Beside chlorine, the molecules N_2, O_2, F_2, CO, CO_2, and C_2H_2 should fulfill this condition.

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