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METHANE DIFFUSION IN ZEOLITES OF STRUCTURE TYPE LTA IN DEPENDENCE ON PHYSICAL AND CHEMICAL PARAMETERS - AN MD STUDY

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Using molecular dynamics computer simulations (MD) the dynamics of kinetic processes in zeolites is discussed on a molecular level. Small changes in lattice parameters can cause large changes in the diffusion coefficient. This has been examined in various simulations employing different interaction parameters. The presence of Na^+, Ca^{++} cations is shown to reduce the self-diffusivity dramatically. The influence of lattice vibrations on the self-diffusion coefficient is found to depend strongly on the structure. Isotopic substitution of methane is examined. The propagator $P(\vec{r},t)$ illustrates the diffusion behaviour of the guest molecules. The process of transport diffusion has been studied by different kinds of nonequilibrium simulations.

1. INTRODUCTION

The knowledge of diffusion processes in zeolites is of great technical importance [1–3] and because of their special properties of great scientific interest too. Molecular dynamics computer simulations (MD) [4,5] that give insight into the dynamics of kinetic processes in zeolites will be discussed on a molecular level. Furthermore, MD allows variations in the system parameters which are not possible in experiments. So, interrelations and dependencies can be examined. The goal of our investigations is to understand the experimentally observed behaviour of diffusing guest molecules in zeolites [2,6] by MD simulations and to derive more general knowledge from our results. This can be done either by theoretical derivations or by the insight into fundamental dependencies obtained from simulations with varying system parameters.

In MD simulations, the trajectories of several hundreds up to several thousands of particles are calculated by computer integration of Newton's law. The results are assumed to be representative for large systems. During the last 4 decades, for a multiplicity of systems this conception has proved to be most successful [4,5]. Methods of statistical physics and computer simulations can form a very useful bridge between the movements of single particles and macroscopic results.

The investigation of diffusion in zeolites by MD simulations started as late as 1988 [7]. In the meantime, however, a lot of papers about this subject have been published and there is still an increasing interest (e.g. [8–18] and references therein). For our investigations, we have used NaCaA zeolites and their cation-free analogue ("ZK4") [2,5,11].

2. SIMULATIONS

2.1. Technical details

The MD simulations were carried out by means of the velocity Verlet algorithm [4,5] with up to 6 000 000 time steps of 5 fs and 10 fs, respectively. The basic MD box contains 8 up to 343 large cavities with values for the total number of guest molecules between 8 and 448. The interactions have been modelled by the Lennard-Jones (LJ) (12,6) potential

$$U(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}, \tag{1}$$

with ϵ as the potential minimum and σ defined by $U(\sigma) = 0$. This spherical potential has been adopted even for methane because it is a very good approximation [19].

In the case of the zeolite NaCaA the interaction with the cations must be added. As the methane molecule is neutral and has a vanishing dipole moment only the polarization interaction between cations and methane must be taken into account. This is done in the same way as in [13] following a method proposed by Ruthven [5,20].

Using the conventional microcanonical MD ensemble the self-diffusivity is calculated while more generalized nonequilibrium (NEMD) ensembles are used to examine the diffusion under nonequilibrium conditions (transport diffusion).

2.2. Potential models A, B

It has been shown that the choice of the σ parameter of the Lennard-Jones potential for the methane oxygen interaction has a dramatic influence not only on the value of the diffusion coefficient but also on its concentration dependence [10]. The σ parameter was changed within the range of values used in the literature for this quantity. Now, these examinations have been extented to a large range of different temperatures and concentrations of guest molecules.

As in [10] we use the two different potentials (A,B) based on the following sets of potential parameters. Model A: CH_4-CH_4: $\sigma = 3.817$ Å, $\epsilon = 1.232$ kJ/mol; CH_4-O: $\sigma = 3.14$ Å, $\epsilon = 1.5$ kJ/mol; CH_4-Si: $\sigma = 2.14$ Å, $\epsilon = 0.29$ kJ/mol [21]; Model B: as model A, but with CH_4-O changed to $\sigma = 3.46$ Å, $\epsilon = 0.81$ kJ/mol.

Figures 1 and 2 provide an impression of the shape of the potential surface, in particular with respect to the different behaviour in the vicinity of the window for the two models. One can see that the potential values are high in the center of the large cavity and, of course, at the repulsive walls. The potential has a minimum in the window in model A and in front of the window in model B where it has a saddle point in the center of the window. This threshold reduces the diffusivity in model B.

2.3. The diffusion coefficient and the propagator

By the evaluation of different moments of the displacement of a given guest molecule it has been shown already that the migration of guest molecules within the zeolite ZK4 is governed by the diffusion equation [9].

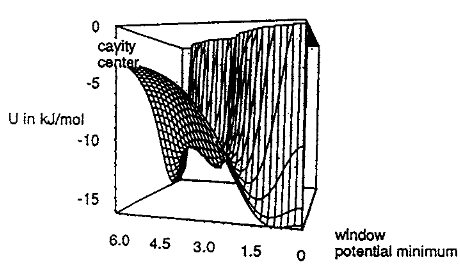


Figure 1. Potential energy in ZK4 (set A).

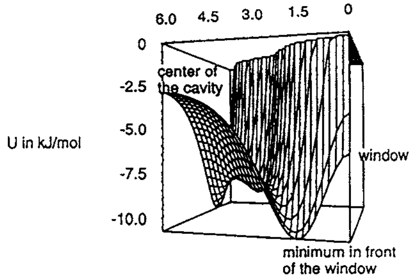


Figure 2. Potential energy in ZK4 (set B).

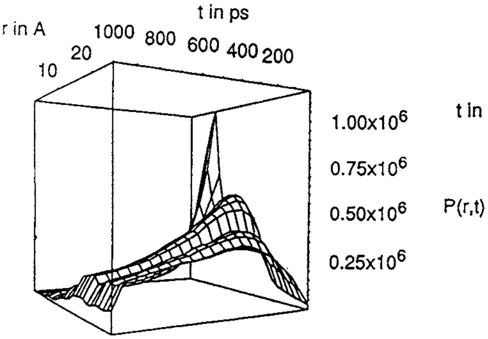


Figure 3. The Propagator P as a function of r and t. The distance r is given in Å and the time t in picoseconds.

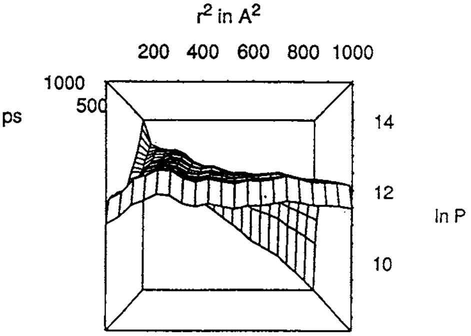


Figure 4. Same as before but the logarithm of P is shown as a function of r^2 at different times ($r_0 = 0$).

An alternative and more direct way is to look at the propagator. The propagator $P(\vec{r}, t)$ describes the probability to find a particle at site $\vec{r}$ at time t if the same particle was at site $\vec{r}_0$ at $t = 0$. In the case of normal diffusion with a diffusivity D one has [2]

$$P(\vec{r}, t) = (4\pi D t)^{-3/2} \exp\left\{\frac{-(\vec{r} - \vec{r}_0)^2}{4Dt}\right\}. \tag{2}$$

The comparison of the shape of the propagator evaluated in an MD run with the theoretical expression eq.(2) provides a straightforward means to check, whether the considered transport phenomena are in fact subjected to normal diffusion. In this case, in particular, a plot of $\ln P$ versus r^2 should show straight lines for each fixed t. The slope of these lines would be proportional to t^{-1}. In this way, normal diffusion can be distinguished from anomalous diffusion which can quite easily be observed e.g. in single file systems [15]. Figure 3 gives a representation of the propagator as resulting from MD simulations. The agreement with the theoretical shape is satisfactory, if one takes into account that the r

dependence shows a structure strongly related to the zeolite dimensions (cavity diameter about 12 Å). For sufficiently large displacements the plot of $\ln P$ versus r^2 in figure 4 shows straight lines with slopes $\sim t^{-1}$ for each t as to be required in the case of normal diffusion.

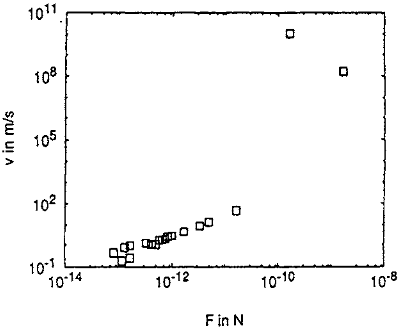


Figure 5. Stream velocity $\overline{v}_z$ as a function of external force F (in Newton).

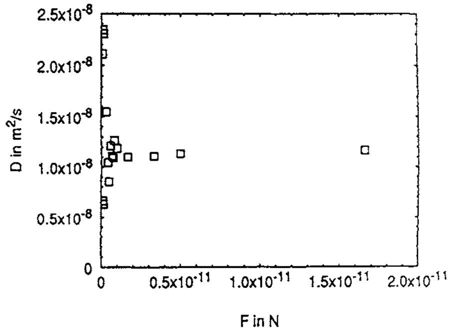


Figure 6. Diffusion coefficient D as a function of external force F (in Newton).

2.4. Nonequilibrium Simulations

In [14] we compared the self diffusivity with the transport diffusivity obtained from the simulation of a density gradient. An alternative way to examine the transport diffusivity is to employ an external field [23] as it was done in [16] for the diffusion of methane in silicalite . The constant external force F, assumed to act in direction of the z axis, causes a stationary particle stream density $j = n\overline{v}_z$ where n is the particle density and $\overline{v}_z$ is the average particle velocity. For sufficiently small forces, $\overline{v}_z$ should be proportinal to F:

$$\overline{v}_z = BF. \tag{3}$$

What is determined in this kind of simulation is the mobility B, not the diffusivity. But linear response theory [24] connects the mobility B with the equilibrium fluctuations of J_z by

$$B = \frac{1}{Nk_BT}\int_0^\infty \mathrm{d}t \langle J_z(0)J_z(t)\rangle_{eq}, \tag{4}$$

where $J_z = \int j\mathrm{d}^3r = \sum_j v_j$ and eq means averaging over an equilibrium ensemble. The self diffusion coefficient is given by Kubo's formula [24],

$$D_0 = \frac{1}{N}\sum_j \int_0^\infty \mathrm{d}t \langle v_{zj}(0)v_{zj}(t)\rangle_{eq}. \tag{5}$$

Defining the corrected diffusivity $D_c = Bk_BT$ we find

$$D_c = \frac{1}{N}\sum_j\sum_k \int_0^\infty \mathrm{d}t \langle v_{zj}(0)v_{zk}(t)\rangle_{eq}. \tag{6}$$

The difference between D_c and D_0 is seen to be caused by cross terms $v_{zj}(0)v_{zk}(t)$, $j \neq k$. Figure 5 shows the mean stream velocity $\bar{v}_z$ as a function of the constant external force F acting on the methane molecules. Evidently, the upper limit of the linear regime was reached at about 10^{-11} N. Linear response theory states the equivalence of mobility and diffusivity only in the limit of vanishing force. Small values for F are therefore desirable. However, as F becomes smaller fluctuations increase dramatically (see figure 6) thus limiting the method's applicability.

3. RESULTS AND DISCUSSION

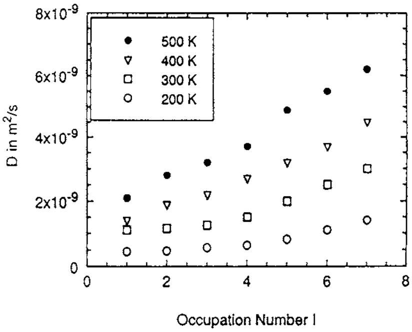


Figure 7. Diffusion coefficient D of methane in ZK4 (set B) as a function of T and I.

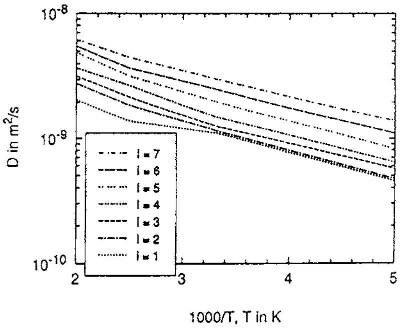


Figure 8. Arrhenius law: Methane in ZK4 (Parameter set B).

3.1. Influence of change of potential parameters on the diffusion

A comparison is made between the results for ZK4 (Set A) which have been published already for a wide range of temperatures and concentrations [10], and the corresponding results for set B (figure 7). For all temperatures, the diffusion coefficient in model B increases with increasing loading in contrast to the corresponding relationship in model A. The latter one is similar to the dependency that one would expect in bulk systems.

Figure 8 looks very similar to the corresponding one for set A [10,11] showing in good approximation a linear dependency of $\log D(I,T)$ upon T^{-1} for all loadings I. Therefore, the validity of the Arrhenius law

$$D(I,T) = D_0(I)\exp\left\{-\frac{E_0(I)}{k_B T}\right\} \tag{7}$$

can be assumed. A comparison of the corresponding pre-exponential factors D_0 and activation energies E_0 of both models can be found in table 1.

The different diffusion behaviour of the guest molecules in both models was illustrated by trajectory studies [10]. It turned out that for higher concentrations the diffusing particles can more easily penetrate into a window. This effect that increases the diffusivity is particularly important in the case of narrow windows because of collective effects.

Table 1
Pre-exponential factor D_0 and activation energy E_0.

	model A		model B	
	D_0 in 10^{-8}m^2/s	E_0 in kJ/mol	D_0 in 10^{-8}m^2/s	E_0 in kJ/mol
I = 1	2.09	1.7	1.38	3.87
I = 2	1.99	1.6	1.52	4.34
I = 3	2.24	2.0	1.52	4.83
I = 4	2.24	2.2	1.13	4.84
I = 5	2.25	2.4	0.92	4.70
I = 6	2.45	2.9	0.84	4.87
I = 7	2.26	3.2	0.51	4.08

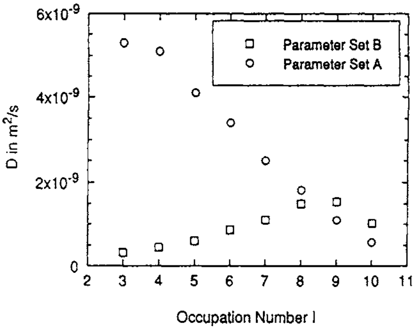


Figure 9. Diffusion coefficient D in ZK4 at 173 K. Comparison of model A and B.

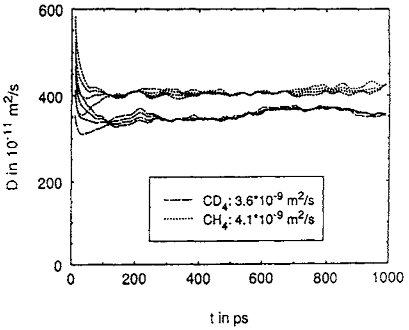
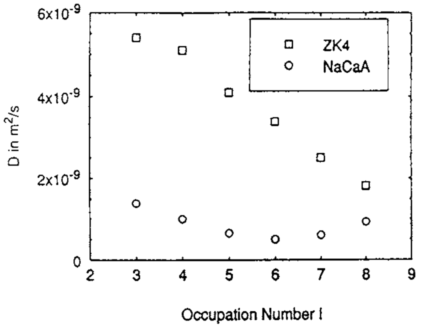


Figure 10. Diffusion of CH_4/CD_4 in ZK4 (set A, 300 K, I = 3).

A second effect, the repulsion back into the cavity which a molecule is just leaving is nearly the same for both models and depends therefore mainly upon the density. The combination of the two effects results in the increase of the diffusion coefficient with increasing loading in model B (see figure 9). At high densities it appears that the diffusion coefficient is higher for model B which has a smaller window diameter. This surprising result might be referred to collective effects of the guest molecules within the cavity at high densities.

3.2. Diffusing CD_4 compared with CH_4

As the bond length C-D is shorter by 4 per mille than that of C-H the CD_4 molecule is smaller than CH_4. The diffusion coefficient decreases with increasing particle mass but increases with decreasing diameter. So, the question arises whether the diffusion coefficient of CH_4 or CD_4 is larger. Figure 10 shows that D is smaller for CD_4 in model A. The ratio of the two D values is close to the square root of the mass ratio. This means that the size effect is negligible in this case.



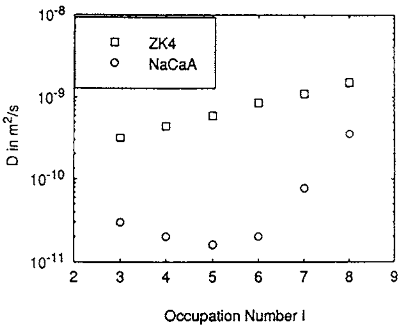


Figure 11. D of methane in ZK4/NaCaA (T = 173 K, parameter set A).

Figure 12. D of methane in ZK4/NaCaA (T = 173 K, parameter set B).

3.3. Influence of exchangeable cations

We have shown that the polarization interaction between the neutral methane and especially the Ca^{++} cation is very strong and diminishes the diffusion considerably [11-13]. This was also confirmed experimentally [22]. The different dependence of the diffusion coefficient D of methane molecules in ZK_4 and NaCaA on the average number of guest molecules per cavity, I, for the models A,B is shown in the figures 11,12.

3.4. Influence of lattice vibrations

Suffritti and Demontis found that lattice vibrations can have a large influence on diffusion in zeolites with narrow windows [17,18]. Comparing the results obtained with fixed and vibrating framework it was found, that this effect depends strongly on the zeolite structure [26]. This has been examined by a comparison of calculations with fixed and vibrating framework.

4. CONCLUSIONS

Computer simulations and statistical physics give excellent possibilities to understand and verify experimental results. These methods represent a most powerful tool for future studies of such fundamental phenomena like adsorption, diffusion and catalysis in zeolites.

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