

An MD study on the diffusion of methane in a cation-free LTA zeolite. Illustrations and new results

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Abstract

The diffusion coefficient for a cation-free zeolite of type LTA is examined employing a widely used set of interaction parameters. A comparison with earlier results that have been obtained with an alternative parameter set enables conclusions concerning the parameter dependence of the observed physical properties. The diffusion behaviour of the guest molecules is illustrated by representations of concentration profiles and the propagator.

1. Introduction

Zeolites as representatives of porous solids (on a molecular level) find various applications for industrial purposes, e.g. as molecular sieves or catalysts [1–3]. In view of this economic background, the examination of the mechanism of transport processes in zeolites is of extraordinarily high interest.

Molecular dynamics (MD) simulations are well suited to understanding diffusion phenomena [4,5]. Beside experimental investigations [2,3], in the last decade several MD investigations, dedicated to the diffusion of guest molecules in zeolites (e.g. Refs. [6–22] and papers cited there), have been published. MD simulations may serve as a ‘bridge’ between the theory of particle kinetics and the phenomenological point of view of experiments. The ability of MD simulations to vary individual parameters of the zeolitic structure can substantially support an understanding of the elementary process and mechanisms of molecular transport.

2. The zeolite lattice, interaction potentials

In this letter zeolites of structure type LTA are examined. Their cubic symmetry simplifies the computational handling. A well-known representative of this structure type is the zeolite NaCaA. Studies of the dependence of the diffusion on changes in the structure of the zeolite lattice, represented by variations of potential parameters, are carried out for the cation-free form of LTA, with methane as the considered diffusant. Among technically interesting substances, methane has a particularly simple shape approaching spherical symmetry.

Correspondingly, we use a spherical approximation for the guest molecule [23]. The guest-host interaction is also represented by pure Lennard-Jones potentials, which means that the charges of Si and O are neglected. As there is a balance of charges within the lattice of completely dealuminated zeolites, the resulting electric field within the cavities is weak. For methane which has neither an electric charge nor a dipole mo-

ment we neglect the polarization interaction because of the weak field.

In Ref. [14] we introduced parameter sets A and B corresponding to different potentials found in the literature for the interaction of methane with the lattice oxygen. Insight into the diffusion mechanism can be obtained comparing the physical phenomena resulting from such a variation of parameters. Having treated in Ref. [14] only a special case, in this letter we extend the study to a wider range of temperatures and concentrations of guest molecules.

The diffusion coefficient depends sensitively on the choice of the Lennard-Jones parameter σ in the region between sets A ($\sigma = 3.18 \text{ \AA}$, $\epsilon = 1.4 \text{ kJ/mol}$) and B ($\sigma = 3.46 \text{ \AA}$, $\epsilon = 0.88 \text{ kJ/mol}$) as shown in Ref. [14]. The ϵ value is of minor importance. The question of which parameter set is the most realistic one is still unresolved and parameters beside sets A and B may also be found in the literature. The parameters used by Demontis and Suffritti (e.g. Refs. [18,19]) lead to a potential curve close to that for parameter set B (see Fig. 13 in Ref. [14] and Fig. 2 in Ref. [17]) although their σ value ($\sigma = 3.88 \text{ \AA}$, $\epsilon = 1.8 \text{ kJ/mol}$) is even larger than that of set B. Unfortunately, there are no measurements for the cation-free LTA zeolite. This, the potential parameters can be checked only via comparison of experiments with simulation results for partially dealuminated LTA or for other zeolites e.g. silicalite.

Demontis and Suffritti carried out simulations of methane in a partially dealuminated NaA zeolite using their parameter set mentioned above. They found too small diffusion coefficients in comparison with the experimental data while set A gave better values [20]. However, the authors argue that this does not necessarily lead to the conclusion that parameter set A is the correct one. They assume that the potential model which they used in Ref. [20] overestimates the polarization interaction thus decreasing the calculated diffusion coefficient. With a weaker polarization interaction the discrepancy from experiment for set B could be reduced while set A could yield worse results than those mentioned in Ref. [20]. Therefore, the authors conclude that the best choice for $\sigma_{\text{O-CH}_4}$ is probably an intermediate value between their parameters and set A [20].

The parameters can be checked independently by comparison of Grand canonical Monte Carlo simula-

tions with adsorption measurements [24,25]. These simulations have been performed in silicalite. However, since the electronic structure of O in the lattice is similar, the guest–host O–CH₄ interaction should be the same in all zeolites. According to Ref. [25], a good choice for the Lennard-Jones parameters used for the O–CH₄ interaction is $\sigma = 3.69 \text{ \AA}$, $\epsilon = 0.75 \text{ kJ/mol}$. However, it is also mentioned in this reference that this result is entirely dependent on the choice between different experimental values and that more experiments should be done to decide this question finally. The simulations in Ref. [25] have been done with a rigid lattice. Although the adsorption and diffusion of methane in silicalite (contrary to LTA) seem not to depend sensitively on the effective diameter σ , a somewhat larger value for this parameter could be obtained by the method of Ref. [25] taking into account the flexibility of the lattice [27].

In agreement with the above mentioned arguments of Demontis and Suffritti [20], in this Letter we compare the diffusion coefficients for different concentrations and temperatures in the case of parameter set B with those published earlier for set A.

We have done all simulations for sets A and B with a rigid lattice. Test calculations for the cation-free LTA have shown that neither for set A nor for set B the lattice vibrations have a large influence on the diffusion coefficient. This finding is in contrast to the observation of Demontis and Suffritti who, employing their parameter set (which leads to nearly closed windows), found that lattice vibrations enlarge the diffusion coefficient by more than one order of magnitude [18,19]. It is most likely that this different importance of lattice vibrations is a consequence of the differences in the window diameters as to be discussed in Ref. [26].

3. Simulations

The simulations were done using the velocity-Verlet-algorithm in an MD-box of $2^3 = 8$ (partially $3^3 = 27$) large cavities (α -cages). In the calculation of the forces acting on a guest molecule 576 lattice atoms are taken into account. The number of guest molecules ranges from 1 to 8 per cavity for different MD runs. Periodic boundary conditions have been employed.

The same MD (Fortran) program was used on dif-

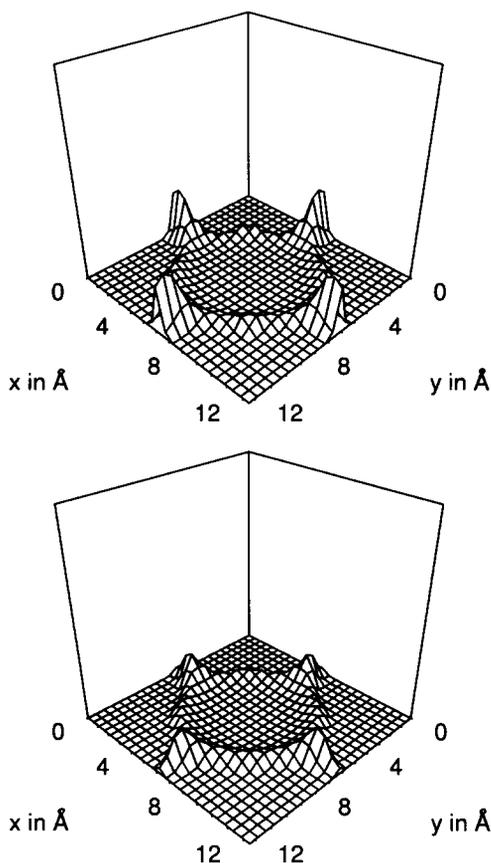


Fig. 1. The concentration profile in the plane $z = 6.1 \text{ \AA}$ containing four windows and the center of a large cavity. Number of guest molecules per cavity (Set A above, Set B below), $I = 3$, $T = 300 \text{ K}$.

ferent hardware platforms. The data were produced on a CRAY-Y-MP at the KFA Jülich, a Convex C3800 at the University of Leipzig and a DEC- α -station at the University of California (Irvine, USA). The time increment for the integration of Newton's equations was 10 fs. Each run consists of a thermalization period of 20 000 steps (200 ps) and the evaluation part with a duration of up to 2 000 000 steps corresponding to 20 ns.

All the values of diffusion coefficients presented in this letter have been obtained by the comparison of different moments of the particle displacements as described in Ref. [13]. This method is an extension of the standard way which is based on an analysis of

the second moment only.

4. Results and discussion

4.1. The density distribution of guest molecules

As an illustration of the different physical situations for parameter sets A and B, Fig. 1 shows the density distribution of guest molecules in the central plane within the zeolite. This plane includes the center of the large cavity and four windows. Each window connecting adjacent cavities is in fact a kind of short 'tube'. On top of Fig. 1 for parameter set A one can see that the density has relatively high values in the windows up to regions beyond the drawing. The highest value is reached near the end of the window 'tube'. The maxima can be seen in front of the window for parameter set B at the bottom of Fig. 1. This corresponds to the potential minima found at these places (cf. Ref. [14]). All these pictures confirm earlier results that the center of the cavity is relatively free from guest molecules [7]. Except at high densities the guest molecules only move along the cavity walls.

4.2. The propagator

An appropriate tool for illustrating the dynamical behaviour of the guest molecules (beside velocity autocorrelation functions, residence times [14], temperature fluctuations [7] and moments of the distribution of displacements [13]) is the propagator. The propagator $P(\mathbf{r}, t)$ describes the probability of finding a particle at site $\mathbf{r}_0 + \mathbf{r}$ at time t if the same particle was at site \mathbf{r}_0 at $t = 0$. In the case of normal diffusion with a diffusivity D one has [2]

$$P(\mathbf{r}, t) = (4\pi Dt)^{-3/2} \exp\left\{\frac{-r^2}{4Dt}\right\}, \quad (1)$$

where the diffusion coefficient is a parameter of this probability distribution, $r = |\mathbf{r}|$. Comparing different moments of this propagator with different powers of the displacement of a given guest molecule it has already been shown that the migration of guest molecules within cation-free LTA is governed by the diffusion equation [13].

The propagator has been shown to result experimentally by Fourier transformation of the spin echo

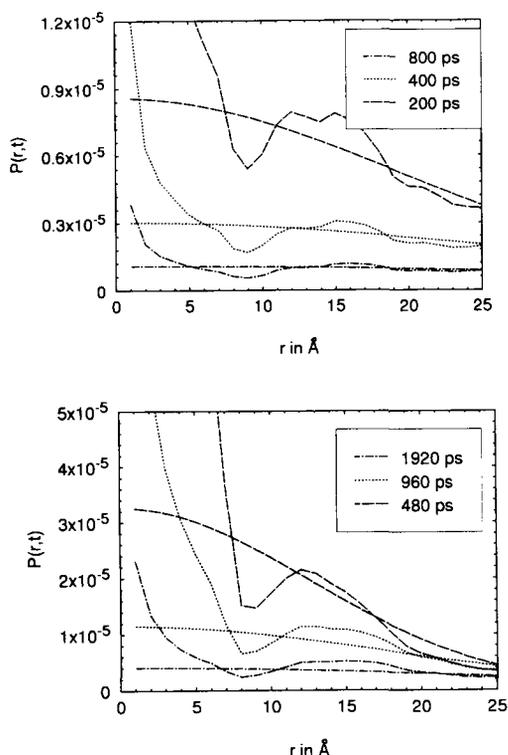


Fig. 2. The propagator $P(r, t)$ from an MD trajectory at different fixed t values (Set A above, Set B below), $l = 3$, $T = 300$ K.

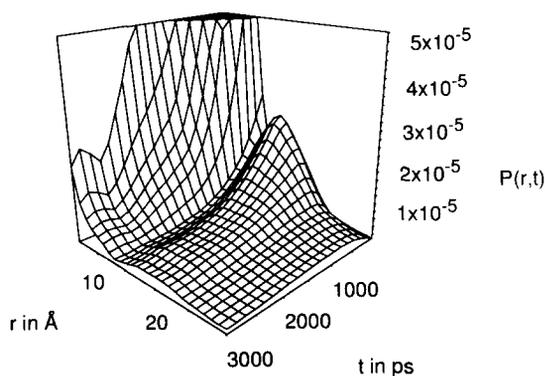


Fig. 3. The propagator as function of r and t . Set B, $l = 3$, $T = 300$ K.

attenuation in pulsed field gradient NMR experiments [28]. This possibility established the fundamentals of PFG NMR for dynamic imaging [29,30]. The propagator may clearly be determined directly from the MD simulations. The comparison of the shape of the prop-

agator evaluated from an MD run with the theoretical expression Eq. (1) provides a straightforward tool for checking 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 be observed, for example, in single file systems, where the slope would only scale with $t^{-1/2}$ [31]. Fig. 2 shows the propagator for several fixed times as a function of the displacement r .

The values from the ideal propagator (smooth lines) given by Eq. (1) are compared with results from MD runs. The latter clearly shows a structure which is connected with the geometry of the zeolite. The observed oscillations correspond to the formation of a relative minimum in the PFG NMR spin echo attenuation observed for molecular diffusion of a liquid in a network of pores formed by the free space in a bed of glass beads [30]. The pore distances of those studies were of the order of a few micrometers. So far, the limited spatial resolution of PFG NMR does not allow similar studies with much smaller pore distances so that presently PFG NMR experiments of this type with zeolites are impossible.

For distances larger than about 12 \AA , which is about the distance of adjacent cavities, the oscillations of the curve from MD around the ideal one become definitely smaller and the two curves approach each other. The larger the time, the shorter the distance where this approach takes place. This corresponds to the well-known fact that the diffusion equation is valid for large times and displacements only [13]. The dependence of P on both the time t and the displacement r is illustrated for case B in a three dimensional plot in Fig. 3. For the sake of clarity, all data points with $P(r, t) > 5 \times 10^{-5}$ are left out of the representation. Eq. (1) may be easily used to determine the time t_M at which for a given value of r , $P(r, t)$ passes a maximum. It is noteworthy that t_M results in exactly the time for which the root mean-square displacement coincides with the value of r ; i.e. $6Dt_M = r^2$. This maximum can be seen in Fig. 3 for the case $r = 25 \text{ \AA}$ at the lower right-hand border of the drawing for an observation time of approximately 500 ps. In Fig. 4 $\ln P$ versus r^2 is given for the same system. As expected, straight lines appear at large times only. It can be seen

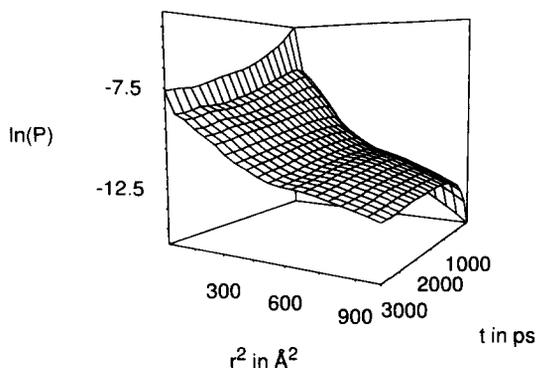


Fig. 4. $\ln P$ versus r^2 . Set B, $l = 3$, $T = 300$ K.

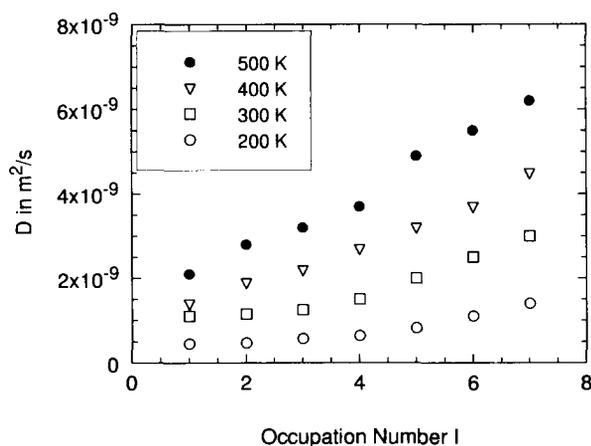


Fig. 5. D as a function of the concentration of guest molecules and temperature.

that the slope decreases with increasing t values since only in this time regime the propagator is sufficiently well approached by a Gaussian.

4.3. Diffusion coefficients as functions of loading l and temperature T for parameter set B

Evaluating the diffusion coefficient D as a function of the concentration of guest molecules and of the temperature we find the values displayed in Fig. 5. The $D(I, T)$ values increase with increasing concentration of guest molecules in contrary to those in the case of set A [14]. From trajectory studies, a histogram of the residence times of particles and from the velocity autocorrelation function we could show that two effects govern the diffusion mechanism.

The first one is that at low densities a particle which approaches the inlet of the window in most cases hits one of the surrounding oxygens and is reflected back into the cavity. At higher densities collective effects enhance the probability of penetrating into the window.

The second effect appears at the outlet of the window. A particle that has passed the “tube” called the window sometimes meets at the outlet another particle just passing the region in front of the window. Then the particle in the window is often pushed back into the former cavity.

The first effect which enhances the diffusion coefficient with increasing density is the more important the narrower the windows. The second one which diminishes the diffusion with increasing density does not depend upon the window diameter. Thus, the relative importance of the two effects should change with changing window diameter. The first one should be more important in zeolites with narrower windows. This is in agreement with the concentration dependence of D found in Ref. [14] and in Fig. 5.

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