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An MD study on the diffusion of a mixture of methane and xenon in silicalite

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Abstract

The diffusion tensor of a mixture of methane and xenon in silicalite is calculated using molecular dynamics methods. For a constant total number of guest molecules per unit cell the ratio methane/xenon is varied from pure methane to pure xenon in order to examine the special properties of diffusion in a mixture. The diffusion of methane is found to be slowed down to the level of xenon diffusion for high xenon quotas in the mixture, while the xenon diffusion is nearly unaffected by a high methane quota. © 1997 Elsevier Science B.V.

1. Introduction

For two reasons zeolites play an important role in the research of diffusion processes on a molecular level. From the theoretical point of view their well-defined crystal structure helps understanding elementary transport processes in porous media [1]. From the practical point of view the wide field of industrial applications, e.g. as molecular sieves, catalysts or ion exchangers [2], make zeolites an important field of research.

Molecular dynamics (MD) simulations have proved to be a helpful tool in understanding diffusion phenomena [3,4]. Especially the abilities of MD simulations for examining data on a molecular level and changing parameters over a wide range make MD simulations a useful supplement to experiments.

2. The silicalite lattice, the computational model

Silicalite is the aluminium-free and therefore cation-free variant of the zeolite type ZSM-5. The symmetry group of silicalite is Pnma with cell parameters $a = 20.07$ Å, $b = 19.92$ Å and $c = 13.42$ Å [5]. In silicalite there are two types of channels. One type is parallel to the y-direction and the other type follows a zigzag path with the main direction parallel to the x-axes. These two types of channels form a three-dimensional network by a special way of connecting each other. The zigzag channels oscillates in the z-direction, which can be used for a propagation there by changing the channel type at the cross-sections: For a movement in z-direction of half a unit cell length it is necessary to follow the channel sections a, b and c in Fig. 1. The two channels have

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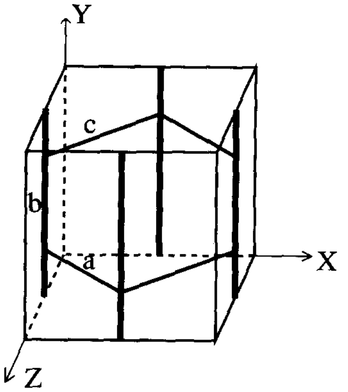

Fig. 1. Schematic view of the channel system within one unit cell of silicalite.

a similar size, the channels in y-direction, called straight channels, have a slightly elliptical cross-section of 5.3 × 5.6 Å and the zigzag channels of 5.1 × 5.5 Å. These channels do not show any narrow sites, therefore the system is not very sensitive to small changes neither in the structure nor in the interaction parameters. Accordingly we used a rigid framework because previous studies in silicalite with rigid/flexible framework led to similar results with regard to the diffusion coefficient [6–8].

For the interaction we use 12–6-Lennard-Jones (LJ) potentials in the form of

$$U_{ij} = 4\epsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]. \qquad (1)$$

Methane is modeled by a simple spherical potential, as in most MD simulations with methane, because the tetrahedral shape of the methane molecule is quite similar to a spherical shape. The spherical potential has proved to be a good enough approximation to the five-center LJ-potential [9] and makes the simulation less time consuming. The used LJ-parameters are given in Table 1. The parameters are taken from literature, wherever possible. For the interaction CH_4–CH_4 and CH_4–O they are taken from [8], for Xe–Xe and Xe–O from [10] and the parameters for the Xe–CH_4 interaction are calculated by the rule of Lorentz-Bertelot [11] from the CH_4–CH_4 and the Xe–Xe parameters:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \qquad (2)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii} * \epsilon_{jj}}\,. \qquad (3)$$

Table 1
Lennard-Jones parameters

	CH_4–O	CH_4–CH_4	CH_4–Xe	Xe–Xe	Xe–O
σ_{ij} (Å)	3.2140	3.7300	3.8970	4.0640	3.2960
ϵ_{ij} (kJ/mol)	1.1080	1.2300	1.5166	1.8700	1.6787

The interaction with the silicon atoms of the lattice is, as usual, neglected because the silicon atoms are not situated close to the channels and the corresponding LJ-interaction is weak compared to the interaction with the oxygen. As a test of this approximation we calculated potential maps of methane is silicalite with and without the silicon atoms. These potential maps were nearly identical, therefore it is justified to neglect the silicon atoms [12].

3. Simulation

The simulations were done using the *velocity Verlet* algorithm with a time step of 10 fs. Each run contained a thermalization part of 10000 steps (100 ps) and an evaluation part of 500000 steps (5 ns). The MD-box contained 128 guest molecules, equivalent to 16 unit cells for a loading of 8 molecules per unit cell or equivalent to 8 unit cells for a loading of 16. All simulations were carried out for a temperature of $T = 300\,K$. The MD program (Fortran) ran on a CRAY-M94 at the KFA Jülich. We calculated the diffusion coefficients for the three main directions x, y and z and an overall diffusion coefficient $D = \frac{1}{3}(D_x + D_y + D_z)$ using the first four moments of displacement according to [13].

4. Results and discussions

The computed values for pure methane and pure xenon diffusion show that diffusion of methane is much faster than diffusion of xenon in silicalite. In different physical situations, this difference lies between a factor 5 and a whole order of magnitude (see Figs. 2–4). We found that the different behaviour

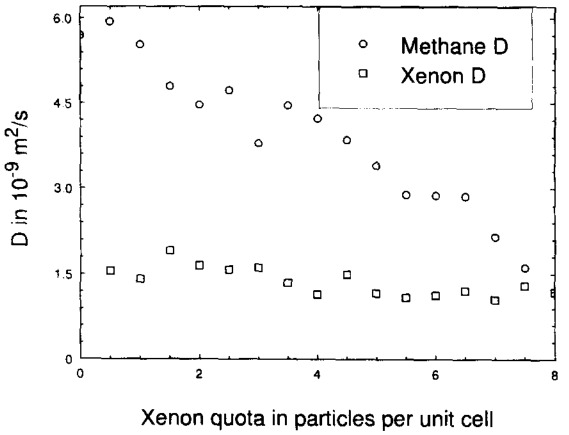

Fig. 2. The diffusion coefficient for different mixtures of xenon and methane with a constant overall loading of 8 particles per unit cell (arithmetic mean of the x-, y- and z-direction).

was due to the mass ratio xenon/methane and to the different LJ-parameters, especially the different ϵ-parameters of the LJ-interactions Xe–O and CH_4–O, and both reasons are of similar importance (see [12]). The simulations with eight guest molecules per unit cell (Fig. 2) show that xenon atoms obstruct diffusion stronger than methane molecules. Having the same total amount of guest molecules in different mixtures, the diffusion coefficient decreases with increasing quota of xenon. This effect is visible for the diffusion coefficient of xenon but much more obvious for methane. The methane diffusion coeffi-

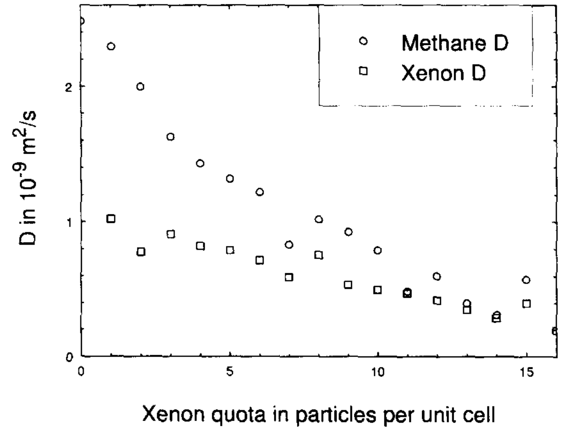

Fig. 3. The diffusion coefficient for different mixtures of xenon and methane with a constant overall loading of 16 particles per unit cell (arithmetic mean of the x-, y- and z-direction).

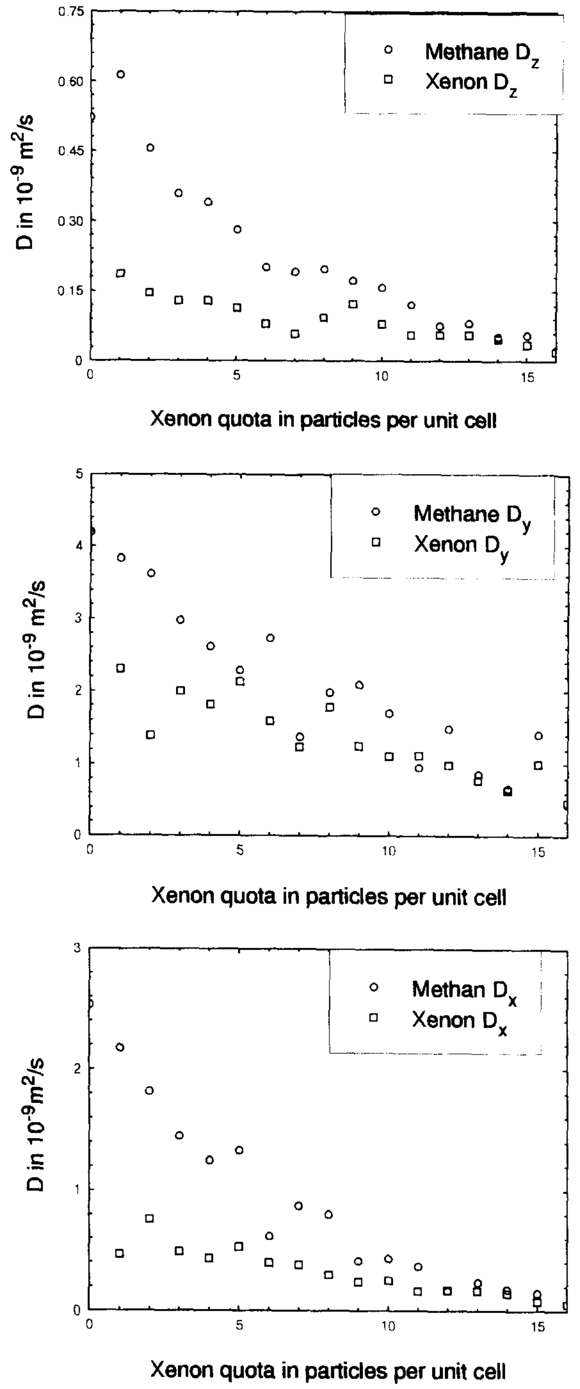

Fig. 4. The diffusion coefficient for the different directions for a total loading of 16 particles per unit cell.

cient falls from about $D = 6 \times 10^{-9}$ m^2/s for pure methane to less than $D = 2 \times 10^{-9}$ m^2/s for nearly pure xenon, while the diffusion coefficient for xenon shows only a slight decrease. We would like to stress the fact, that the diffusion coefficients of methane and xenon are nearly the same for high xenon loadings, while for high methane loadings the xenon diffusion coefficients are much smaller than the methane diffusion coefficients.

The Figs. 3 and 4 show the results of the simulations with a loading of 16 particles per unit cell. For low xenon loadings the results are very similar to the shown above case. The diffusion coefficients of methane decrease with increasing xenon quota. At about nine xenon atoms per unit cell, the diffusion coefficients of methane and xenon are nearly at the same level. Towards the pure xenon end the diffusion coefficients still keep on decreasing, although not as fast as near the pure methane end of the simulation series.

The different directions show a similar behaviour, but on different scales of magnitude (Fig. 4). The diffusion coefficient D_y is about 1.5 times larger than D_x, and D_x is about five times larger than D_z. A more detailed study of the anisotropy of the diffusion in silicalite will follow in [12]. In this work there will be a comparison of our simulated values with the jump model of Kärger [14].

The reason for the very strong influence of the slower xenon atoms on the faster methane molecules is found in the topology of the channel system. The diameter of the channels is too small to allow a passing of the particles within the same channel, therefore the xenon atoms barricade the channels for the methane molecules. With increasing xenon quota more and more channels get blocked and from eight or nine xenon atoms per unit cell nearly all channels are occupied by xenon atoms and the methane molecules can only move within a cage of nearest xenon neighbours. Therefore the methane molecules can no more diffuse faster than the xenon atoms, they only rattle within this cage.

Up to now it is not possible to compare these results with experimental values, as there is no experimental data for diffusion of mixtures in zeolites. Therefore we will measure the same system with PFG NMR in cooperation with Professor Kärger (Leipzig) and present the data in Ref. [12].

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