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The importance of various degrees of freedom in the theoretical study of the diffusion of methane in silicalite-1

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Abstract

The self diffusion coefficient of methane in silicalite-1 is influenced by the flexibility of the lattice unlike the self diffusion coefficient of methane in the cation-free zeolite of type A. In the present paper, besides the influence of lattice vibrations on this process, the influence of internal vibrations of the methane molecule and the applicability of several spherical models of this molecule are examined. The method of moments [Chem. Phys. Lett. 198 (1992) 283] is generalized to anisotropic diffusion.

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1. Introduction

The examination of diffusion processes in zeolites is a task of increasing interest because of the great technical importance of several types of zeolites [2]. Additionally, this examination is of great scientific interest too because of the very special properties of these porous solids.

In the present paper, some aspects of the dynamics of molecular motion and of the coupling between kinetic processes in zeolites will be discussed on a molecular level using molecular dynamical computer simulations (MD). At first, all degrees of freedom are taken into account including the vibrational and rotational degrees of freedom of the diffusing guest molecules and the lattice vibrations. The results are compared with those of runs with rigid five centers methane molecules and/or rigid lattice. Finally, some spherical model potentials for the methane molecules are tested; in these calculations the methane molecules are replaced by "Lennard Jones molecules" with the methane mass.

Discussions about the importance of the lattice flexibility have been going on since 1971. In [3], a case was examined experimentally in which inert gas atoms could pass even the small

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windows of sodalite cages at high temperature. An explanation cannot consider only the thermal window size fluctuations (i.e., the lattice flexibility) because at higher temperatures the higher kinetic energy of the diffusants enables them to overcome more easily energy barriers even in a rigid lattice. According to [4] the diffusion coefficients of inert gases in silicon sodalite calculated by transition-state-theory (TST) are larger by several orders of magnitude for the flexible lattice than for the rigid one. The comparison of results obtained from theory in [4] with experimental values must be viewed with great care as the calculated quantities depend strongly upon the choice of the potential parameters used. For example, in [5] it could be shown that the self diffusion coefficient found in MD simulations for methane in the cation-free A zeolite varied by nearly two orders of magnitude when different sets of potential parameters from the literature were used.

In [6], the influence of the lattice flexibility on the diffusion of different guest molecules in various zeolites (e.g., of methane and xenon in silicalite) was investigated by a Langevin equation treatment. The conclusion for methane in silicalite-1 was that lattice vibrations yield a negligible driving force for this system.

In [7], it was shown that the lattice vibrations have a remarkably small influence on the jump rates between different adsorption sites of benzene in the NaY zeolite. It was concluded that the internal degrees of freedom of the molecule act as a heat bath that is sufficient for thermalization even for this system with high energy barriers.

There are mainly two effects by which lattice vibrations in MD simulations may act on the diffusing particles. The first one is the steric effect and the second one is the exchange of energy between migrating molecules and the lattice.

As the diameter of windows and channels in zeolites changes periodically in time due to the lattice vibrations the height of diffusion barriers fluctuates. We call this the steric effect of lattice vibrations. As shown in [8,9], the histograms of the observed window diameters are symmetric with respect to the average values. Therefore, an increase of the mobility of diffusants by larger windows and an decrease by smaller windows both appear with the same probability. However, it is not a trivial question if this symmetry leads to a vanishing "over-all" effect in all cases.

Due to the second, the energetic effect, the vibrating lattice acts as a heat bath for the diffusing molecules. The relaxation of the fluctuations of the kinetic energy of diffusing particles by energy exchange with the lattice is much stronger than the relaxation caused by the mutual energy exchange of the guest molecules [9,10].

Nevertheless, even the mutual thermalization of the guest molecules turned out to be very effective even at such low concentrations as $I = 1$ in a simple rigid model (no lattice vibrations, no internal vibrations or rotations of the adsorbed molecules) of methane diffusing in the cation-free zeolite LTA [11]. I is the total number of guest molecules divided by the number of cavities in the A–zeolite. The spatial particle density distribution, obtained from these MD runs, agrees nearly perfectly with that of a Metropolis Monte Carlo Simulation carried out for the same temperature and the same concentration of guest molecules. Also, the spatial distribution of the kinetic energy and the fluctuations of the one particle kinetic energy agree well with those of a canonical ensemble. When the mutual interaction of the guest molecules was switched off, then this agreement vanished. So, the mutual interaction was identified to be the reason for the (even local) thermal equilibration [11].

A flexible lattice has been employed in many studies of guest molecule diffusion in zeolites, e.g., in [12–17] and also the flexibility of the diffusing guest molecules is taken into account in some papers. Examples are [12,18]. Treatments of chain hydrocarbons sometimes include even the internal degree of freedom of an isomerization of the guest molecules (e.g., [19]). A rigid lattice has also been used widely. Some examples are [19–24]. The possibility of using a rigid lattice in simulations is of practical importance. This approximation makes it possible to avoid the additional computation of lattice forces and the need of a smaller time step. An even much larger saving of computer time is possible if potential energy and forces for the guest–host interaction for a grid of points are stored in tables and used by interpolating the stored values [20]. Another possibility for simplification of the simulations is the use of empirical analytical functions in the three-dimensional space that reproduce the potential energy and the forces. This was done e.g., in [25,26] for methane in the cation-free A zeolite. Although in [25,26] the simple analytical model is used only for spherical guest molecules the generalization is straightforward: A separate analytical potential must be used for each sort of atoms (or united atoms) in the guest molecules. Up to now, the use of such analytical methods is restricted to simulations in the rigid lattice unfortunately. Such methods are not only useful if very limited computer time is available. In general, even with the best computer facilities they open the door to new challenging applications. It is the feeling of the authors that the task of MD simulations should not be primarily to reproduce known results of experiments with high accuracy. Even to predict such results is not all what simulations can do. Instead they should also help to discover and understand by use of simplified models reasons for and interconnections between interesting effects.

Such a model needs to contain only those details of the real system those are important for the effect under consideration. Which details are really important must be checked by comparison of the discovered effects with experimental reality. Besides its practical importance, the examination of the role of lattice and molecule vibrations in diffusion processes gives insights in the diffusion mechanisms.

In earlier examinations [8,9], it was shown that the lattice vibrations do not effect significantly the self diffusion of methane in a cation-free LTA zeolite. Earlier different findings [14,27] could be corrected.

From the vanishing effect of lattice vibrations on the diffusion coefficient in the cation-free zeolite A, it cannot be concluded that this effect is also vanishing for methane in silicalite-1. In [15], a small influence is found for methane in silicalite-1. But, the mean square displacement is examined in [15] only for a very short length of 30 ps. Demontis et al. [13,28] found for the same system at 298 K that the diffusion coefficient of the guest molecules is about 20% higher with a vibrating lattice than with the rigid one. June et al. [29] found in simulations of xenon in silicalite-1 at 100 K that the self diffusion coefficient is 40% smaller with vibrating lattice than with the rigid one. In [30], another case is mentioned in which the diffusion coefficient decreases in consequence of the lattice vibrations for the diffusion of normal alkanes in zeolites with long one-dimensional channels, like ZSM-12 and Linde-type-L (LTL) zeolites.

In [31], a slightly larger diffusion coefficient (1.33×10^{-7} m^2/s) was found for the rigid lattice than for the flexible one (1.26×10^{-7} m^2/s) for the diffusion of methane in $AlPO_4$-5. A rigid five centers methane was used and the charges of the lattice atoms were taken into account. The authors introduce a method for handling the lattice motion in molecular simulations which utilize the normal vibrational modes in a harmonic crystal approximation.

2. The model and some technical details of the simulation runs

Silicalite-1 is a cation-free zeolite of the structure type MFI [32]. Its lattice consists of silicon atoms and oxygen atoms. The symmetry group of the MFI zeolites is Pnma with cell parameters $a = 20.07$ Å, $b = 19.92$ Å and $c = 13.42$ Å. The channels of silicalite-1 form a three-dimensional network, which consists of two kinds of channels. The intersections between the channels are somewhat similar to cavities in other types of zeolites. The potential energy at the local maximum inside the intersections is about −11 kJ/mol. Fig. 1 shows the channel structure of silicalite-1. One can see the straight channels from top to bottom (y direction) in the picture. The zig-zag channels in the x–z plane are somewhat curved but, also drawn straight in Fig. 1 for simplicity. Their name can be understood if one adds the periodical replica of the unit cell.

A four-center Lennard-Jones potential for methane has been proposed in [33]. However, as we take into account the internal vibrations, all

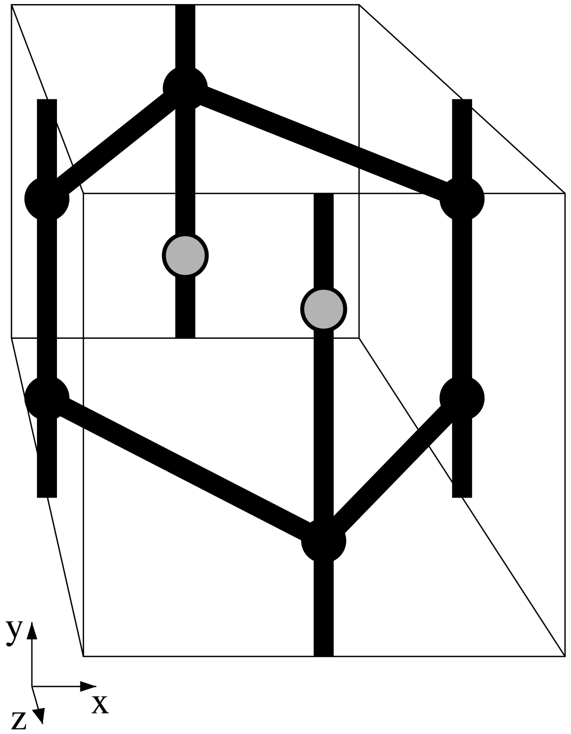

Fig. 1. Topology of channels in the unit cell of zeolites of type MFI, e.g., silicalite-1. The black dots show the intersections between straight channels and zig-zag channels in the unit cell and the grey dots show intersections of the straight channels with zig-zag channels that are outside the unit cell.

atoms must be included. Therefore we use a five-center model with interaction sites on the four hydrogen atoms and on the carbon atom. For the internal degrees of freedom the harmonic valence force model of Bougeard and co-workers [34] is used.

For the interaction between the atoms in different molecules and between the atoms in the CH_4 and the lattice atoms, the MM2 Lennard-Jones (LJ) parameters of Burkert and Allinger [35] have been used which according to [36] yield the best results (compared to some others) for the thermodynamic and transport properties of methane in zeolites. See also our comparison with experiment in Section 3.

All runs have been done in an MD box that consists of two unit cells containing 576 lattice atoms totally. Often the concentration of guest molecules in silicalite-1 is given as guest molecules per channel intersection. Our box includes eight intersections. If we call the number of guest molecules per intersection I, (analogously to the number of guest molecules per cavity in the LTA case) then we have, for example, $I = 1.25$ for 10 methane molecules per MD box.

After an initial run of 10,000 steps for randomizing the system, the temperature has been chosen as in [9] by adjusting the total energy. This is easily done by one single velocity scaling before the main run starts. So, the knowledge of the $T(E)$ dependence is sufficient to achieve any wished temperature. The curve for the $T(E)$ dependence is created from some shorter test runs and this curve is improved after each long run, successively.

Then, an evaluation part of the MD run of 20,000,000 steps was carried out with an time increment of 0.5 fs. That means trajectories of 10 ns have been evaluated in which the trajectories are completely unperturbed by thermalizing algorithms.

Diffusion coefficients have been evaluated using the first four moments of the displacement as described in [1] for the isotropic case. The extension on anisotropic systems is given below. In [37], it is argued that the self diffusion coefficient as derived from the mean square displacement for guest molecules in zeolites is only an apparent one. The authors argue that the Einstein relation between the self diffusion coefficient and the mean square displacement is derived by assuming a random walk which is not true for the migration of the particles within restricted geometries. Instead, it is well-known that the Einstein relation follows also from the diffusion equation (see, e.g., [1]) and that on a time scale that is large enough to allow the guest molecules to move between different cavities or channels the migration of guest molecules is indeed a random process. On such a time scale, both the diffusion equation and the Einstein relation are applicable [1]. A reliable tool to decide whether this time scale has been reached is provided by the method of different moments of the displacement [1]. The formulas for the anisotropic case are derived in Appendix A of the present paper. The evaluation is done for multiple time

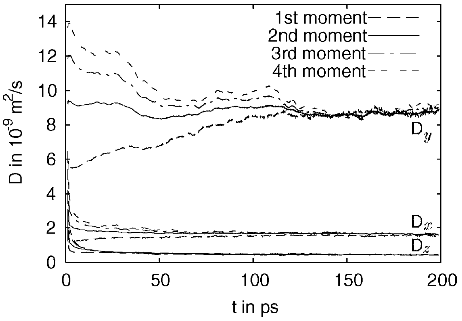

Fig. 2. The diffusion coefficients D_x, D_y and D_z from the first four moments (see Appendix A) of the displacement. The concentration of guest molecules is $I = 4$ methane per intersection and the temperature $T = 300$ K. Lattice and methane molecules are flexible.

origins [38]. As an example, the resulting curves are shown for $I = 4$ and $T = 300$ K in Fig. 2. The kinetic state in which the diffusion equation is valid is reached when the D values obtained from all moments agree which each other, giving a unique D value.

3. Test of the model

In order to check the used implementation and the parameters of the model system described above, a series of runs has been made for one methane molecule per intersection. The measured values given in [39] have been compared with the D values from these MD simulations. D is the trace of the diffusion tensor divided by 3.

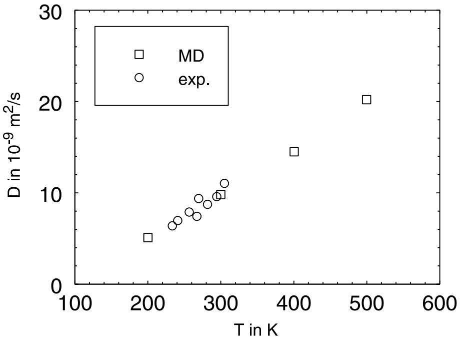

Fig. 3. Comparison of MD results with experiments [39] for $I = 1$.

The simulations have been carried out with flexible molecules and flexible lattice. The results are given in Fig. 3. The agreement is good taking into account the fluctuations in the measured values.

4. Former investigations of methane diffusion in silicalite

The diffusion of methane in silicalite was examined already by several authors. But, the present paper is, to our knowledge, the first systematic investigation that includes both lattice and methane rigid and flexible as well. Most authors have treated methane only in spherical approximation without internal degrees of freedom. The results in Fig. 3 agree well with those of [20,21,40,41], where the molecules are modeled by single Lennard Jones centers and with [36] where atomistic potentials are used.

The value of D found in [37] by simulations (using commercial software) for methane in silicalite-1 at 300 K at infinite dilution is one order of magnitude larger than the value measured at $I = 1$ for the same system [39]. In [15] a value between 0.4 and 1×10^{-9} m^2/s is reported but, the mean square displacement was evaluated over 30 ps only in this work and the statistics are poor. In [42], the authors calculate by MD simulations at 300 K a value $D = 1.6 \times 10^{-8}$ m^2/s for $I = 1$ at 300 K. Demontis et al. [43] report a value of 2.1×10^{-8} m^2/s at 300 K for infinite dilution using a spherical LJ methane and the flexible lattice.

5. New results and discussion

5.1. The self diffusion coefficient for rigid and flexible molecules

Figs. 4–7 show the self diffusion coefficients for the different directions as functions of the temperature at the concentration of one guest molecule per intersection. D_x, D_y and D_z are components of the diffusion tensor and D is the average over all directions. D is also the trace of the diffusion tensor divided by 3. The curves in

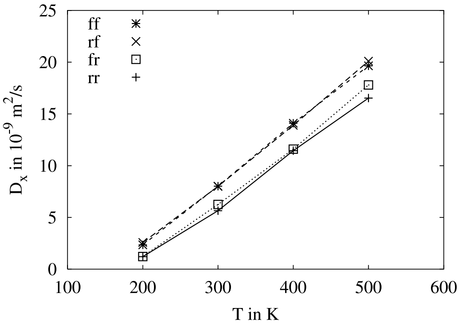

Fig. 4. The diffusion coefficient D_x in 10^{-9} m^2/s for $I = 1$. ff means lattice and molecule flexible, rf means molecule rigid and lattice flexible, fr means molecule flexible lattice rigid, rr means both lattice and molecule rigid.

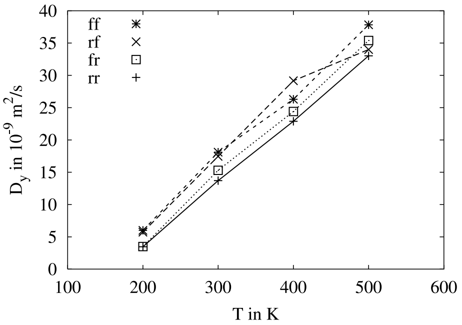

Fig. 5. The diffusion coefficient D_y in 10^{-9} m^2/s for $I = 1$. ff means lattice and molecule flexible, rf means molecule rigid and lattice flexible, fr means molecule flexible lattice rigid, rr means both lattice and molecule rigid.

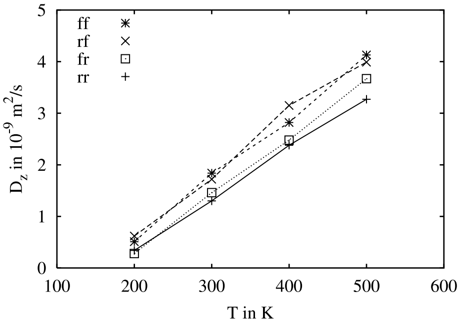

Fig. 6. The diffusion coefficient D_z in 10^{-9} m^2/s for $I = 1$.

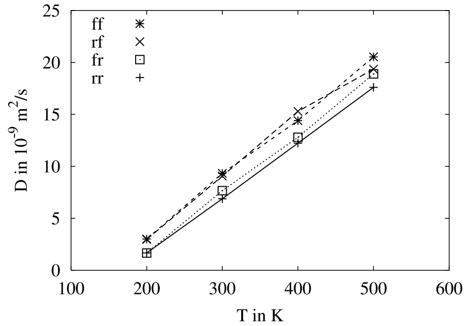

Fig. 7. The average diffusion coefficient D in 10^{-9} m^2/s for $I = 1$.

Figs. 4–7 show that in agreement with Demontis et al. [13,28,43] the lattice flexibility enhances the diffusion coefficient of methane in silicalite-1. Additionally it can be seen that molecule flexibility although also increasing the diffusivity slightly has a much smaller effect.[1]

In Fig. 8, the corresponding D values are displayed for four guest molecules per intersection. The influence of the flexibility of lattice and molecules can be seen to have only small influence on the diffusion coefficients at high loading. This influence turns out (see Fig. 8) to be within the range of fluctuations of the theoretical D values obtained from the MD simulations.

Three runs for the case with the largest fluctuations have been done to get an upper limit on the error bars that should be associated with the individual calculated values. This is the case of rigid methane and rigid lattice at 300 K. The averaged D values for this case and the corresponding error bars are $D_x = (1.42 \pm 0.07) \times 10^{-9}$ m^2/s, $D_y = (1.02 \pm 0.11) \times 10^{-8}$ m^2/s and $D_z = (3.84 \pm 0.10) \times 10^{-10}$ m^2/s and the average over all directions is $D = (4.0 \pm 0.38) \times 10^{-9}$ m^2/s.

5.2. Spectra of lattice and molecule vibrations

For more detailed understanding of the interrelations between lattice movements and molecule migration, the velocity autocorrelation functions (VACFs) of the different atoms belonging to molecules or to the lattice have been evaluated and their Fourier transform are obtained too. The Fourier transforms are given in arbitrary units that

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[1] This conclusion corrects an earlier finding on the effect of molecular flexibility [44].

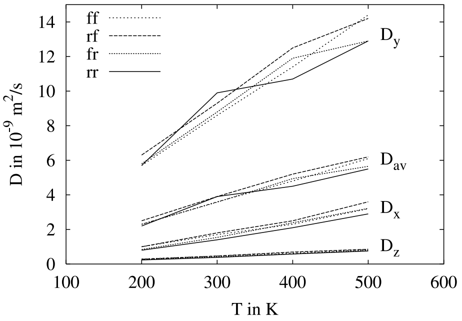

Fig. 8. Diffusion coefficients for $I = 4$. ff means lattice and molecule flexible, rf means molecule rigid and lattice flexible, fr means lattice rigid and molecule flexible, rr means both lattice and molecule rigid.

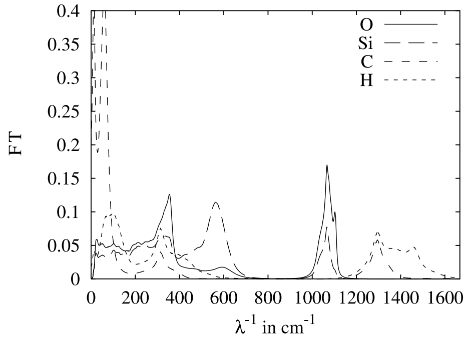

Fig. 10. Comparison of the Fourier transform of the VACFs of all atom sorts involved in the simulation.

originate from the evaluation program COSTRAFO published in [45]. As an example, Fig. 9 shows the VACF and the Fourier transform for the hydrogen atoms at 300 K. The frequency modes appearing at about 1500 and 3000 cm^{-1} in the spectrum agree very well with those found for bulk methane in infrared spectra measurements [46] and also with the frequency spectrum from MD data for methane in silicalite-1 published in [15]. Although in the infrared measurements the Fourier transform of the autocorrelation function of the dipole moment and not a VACF is analyzed, that agreement is not surprising because the dipole moment changes mainly by the movements of the light hydrogen atoms. These frequency regions are, of course, also associated with the normal vibrations of a gas-phase methane molecule [47].

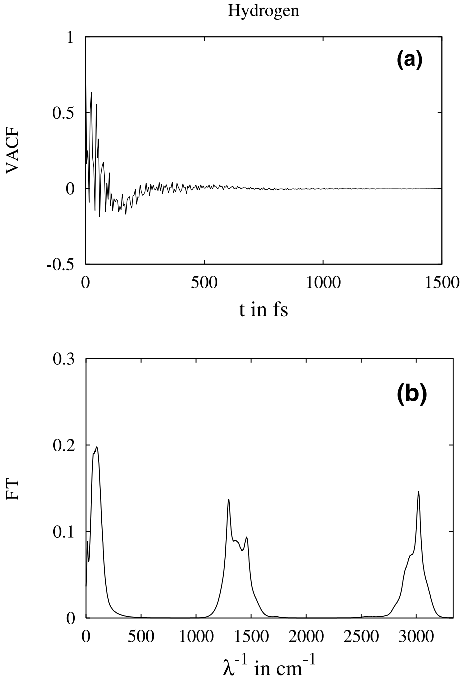

Fig. 9. (a) The velocity autocorrelation function of the hydrogen atom in the methane molecule and (b) its spectrum obtained by Fourier transform.

A comparison of the atomic spectra of the four kinds of atoms in the system in the low-frequency region is shown in Fig. 10. It is seen that all spectra overlap in that region. So some influence of the lattice vibrations on diffusion, as found above, is to be expected.

5.3. Check of the symmetry relation of Kärger

In the paper [48] a rule about the correlations between the components of the diffusion tensor

$$\frac{c^2}{D_z} = \frac{a^2}{D_x} + \frac{b^2}{D_y} \tag{1}$$

has been derived by treating the migration of particles as a sequence of uncorrelated movements. Deviations caused by correlated moves of the guest molecules are examined in [49] for ethane and in [50] for some linear molecules in silicalite-1. In [51], a quantity β is defined that is used in several papers, e.g., [21,51] in order to examine the validity of Eq. (1)

$$\beta = \frac{c^2/D_z}{a^2/D_x + b^2/D_y}. \qquad (2)$$

The rule is found to be fulfilled approximately but with some deviations [21,51] they may reach 100% in some cases. In Table 1 the values of this quantity found in the present simulations using the MM2 potential parameters are shown.

The β values in Table 1 are never smaller than 1.0 but, in most cases they are larger. According to Eq. (2) that means that existing correlations enhance the probability to remain in channels of the same type. The diffusion in z-direction can only occur if there is a sequence of moves through different channel types. β seems to increase somewhat with increasing temperature and also with increasing concentration of guest molecules. But, because of the structure of Eq. (2) β is relatively sensitive with respect to errors in D_z. Therefore, conclusions drawn from Table 1 about the dependence of β upon the temperature or upon the model used, are ambiguous.

In [21] also β values that are smaller than 1.0 have been found in some cases but the majority of results show also β values larger than 1.0. The negative deviations from 1 are within the limits of error. In [21], the guest molecules xenon and methane are represented by spherical models.

In [52] β values that are smaller than 1.0 are found but, this finding should be checked carefully as, in a most recent paper [24], the durations of the runs reported in [52] have been assessed to be too small to get reliable diffusion data. This conclusion is in agreement with our test of the β value given in [52] for a concentration of eight methane per unit cell in silicalite-1 at 300 K. Using the same interaction parameters as in that paper, we found in a test run $\beta = 1.52$, a value larger than one as it should be expected. In [52], a value of 0.6 has been given for this case.

Table 1
The symmetry factor β as defined in Eq. (2)

	β for $I = 1$	β for $I = 4$	T (K)
rr	1.00	1.34	
rf	1.16	1.40	200
ff	1.32	1.30	
rr	1.28	1.43	
rf	1.43	1.46	300
ff	1.12	1.37	
rr	1.40	1.36	
rf	1.43	1.35	400
ff	1.38	1.36	
rr	1.41	1.41	
rf	1.25	1.50	500
ff	1.53	1.42	

5.4. Spherical averaged potentials

Finally, the degrees of freedom that are connected with the rotation of the molecules are removed choosing spherical averaged potentials for the methane–methane and the methane–silicalite-1 interactions. In Fig. 11, the interaction energy of a methane molecule with another methane, a lattice oxygen and a lattice silicon are shown as a function of the center of mass distances. These potentials have been obtained from a run with 32 methane molecules, that means $I = 4$. The run was done with a rigid lattice and rigid molecules at a temperature of 300 K. We will explain the evaluation procedure for the example of the methane–methane interaction. The distances between 0 Å and about 10 Å are of interest. This interval is divided into small subintervals of 0.1 Å. An average value of the interaction potential is calculated for each subinterval. For example, the interval between 2.5 and 2.6 Å can be considered. When-

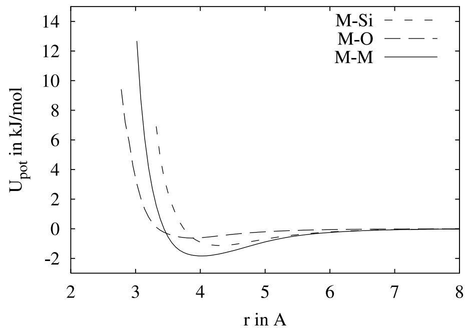

Fig. 11. Effective spherical potentials obtained by the procedure described in Section 5. M–M means methane–methane potential, M–O means methane–oxygen and M–Si means methane–silicon potential.

ever, during the run two CH_4 molecules are found to have a center of mass distance between 2.5 and 2.6 Å then the sum of all mutual potential energies between the atoms of these two molecules is calculated and stored. The average of these values stored throughout the whole run for the interval between 2.5 and 2.6 Å is taken to obtain an effective potential value assigned to the methane–methane distance of 2.55 Å. Lennard-Jones parameters σ and ε are taken from the resulting curves identifying σ with the distance where the interaction potential is zero and identifying ε with the minimum of the interaction potential. The values of the LJ parameters are given in Table 2 named SA MM2 (that means spherically averaged MM2 potential). Three MD runs for $I = 4$ guest molecules per intersection and at $T = 300$ K as before but now using these spherical interaction potentials have been carried out. The results are $D_x = 3.19 \pm 0.08 \times 10^{-9}$ m^2/s, $D_y = 8.88 \pm 0.28 \times 10^{-9}$ m^2/s, $D_z = 0.67 \pm 0.02 \times 10^{-9}$ m^2/s and $D = 4.25 \pm 0.09 \times 10^{-9}$ m^2/s. D means the arithmetic mean over all directions, i.e., one-third of the trace of the diffusion tensor. These diffusion coefficients from SA MM2 are compared in Table 3 with values that result if other spherical potentials from the literature are used. In order to improve the statistics two independent runs, each of them with an evaluation part of two million steps have been carried out. The values given in Table 3 are the mean of two runs.

Table 2
Lennard-Jones parameters σ in Å and ε in kJ/mol for several spherical averaged model potentials

Sorts	σ (Å)	ε (kJ/mol)	
CH_4–Si	3.75	1.13	
CH_4–CH_4	3.44	1.84	SA MM2
CH_4–O	3.37	0.63	
CH_4–Si	0.0	0.0	
CH_4–CH_4	3.73	1.23	B. Smit
CH_4–O	3.694	0.7549	
CH_4–Si	0.0	0.0	
CH_4–CH_4	3.56	0.912	Ermoshin/Engel
CH_4–O	2.985	1.62	
CH_4–Si	2.14	0.29	
CH_4–CH_4	3.817	1.232	Set A
CH_4–O	3.14	1.5	
CH_4–Si	2.14	0.29	
CH_4–CH_4	3.817	1.232	Set B
CH_4–O	3.46	0.81	
CH_4–Si	2.14	0.29	
CH_4–CH_4	3.5	1.232	Set A*
CH_4–O	3.14	1.5	
CH_4–Si	2.14	0.29	
CH_4–CH_4	3.5	1.232	Set B*
CH_4–O	3.46	0.81	

SA MM2 means spherical averaged MM2 as described in the text. B. Smit means the parameter set derived in [53] from adsorption data (heat of adsorption and Henry coefficient). Ermoshin/Engel means the spherical model potential derived in [54]. Set A and set B means that the LJ parameters, named in this way in [5] have been used. In set A* and set B* the CH_4–CH_4 σ has been changed.

An LJ parameter set has been derived by Smit [53] from adsorption data. The corresponding parameters and resulting D values are given in Table 2. In order to reduce the number of parameters that must be adjusted the silicon–methane interaction has been neglected as this is also done in many other simulations in the literature, e.g., [13,14,16,17]. This approximation has been examined and justified in [54]. A set of spherical LJ parameters is also proposed in this paper. Unfortunately, the LJ parameters for the CH_4–CH_4 interaction are not given explicitly in [54]. Therefore, we have calculated them from the polarizability and the susceptibility given in [54] using the Kirkwood–Müller formula [55].

In [5], several LJ parameters found in the literature for the interaction of methane with the lattice oxygen are compared and gathered together into two parameter sets, called set A and set B in [5]. These parameter sets have also been included in the present examination. In order to see the influence of the CH_4–CH_4 interaction the σ parameter of this interaction has been changed in the runs named set A* and set B*.

For the test runs with spherical guest molecules the time step could be chosen to be 5 fs. Therefore, runs of 2 millions steps covered the same total time period of the trajectories as the 20 million time steps for the full MM2 model. Of course, additionally the computational effort per time step was also smaller.

If the * potentials (that are only fictitious potentials for test purposes) are excluded, then

Table 3
Comparison of diffusion coefficients for spherical averaged model potentials with those obtained from the full MM2

Parameter set	D_x	D_y	D_z	D	β	$\langle U \rangle$ (kJ/mol)
SA MM2	3.19	8.88	0.67	4.25	1.58	−21.6
B. Smit	0.90	5.80	0.30	2.15	1.17	−14.6
Ermoshin/Engel	3.06	4.35	0.60	2.67	1.35	−15.6
Set A	2.11	4.89	0.41	2.47	1.63	−17.6
Set B	1.38	7.46	0.40	3.05	1.32	−13.2
Set A*	3.01	5.24	0.57	2.94	1.50	−17.5
Set B*	3.31	8.32	0.67	4.10	1.60	−13.0
Full MM2	1.42	10.2	0.38	4.00	1.47	−22.6

D values are in 10^{-9} $\mathrm{m^2/s}$. Additionally the average potential energy per guest molecule $\langle U \rangle$ is given.

among the examined spherical potentials the spherically averaged MM2 (SA MM2) potential yields the best agreement in D with the values obtained from simulations that employed the full MM2 potential this value being 6% higher than that which resulted from full MM2 potential. It should be emphasized that the parameter set derived in [53] from thermodynamic data reproduces very good thermodynamic properties of the system but not D as can be seen in Table 3. Of course this potential was not designed to yield diffusion data but, it is interesting to see another example of the well-known fact, that potential models, that yield one property of the system well, may fail to reproduce other properties.

The average potential energy per guest molecule $\langle U \rangle$ is also given in Table 3. In [54], the heat of adsorption $H = \langle U_1 \rangle - RT$ is given to be 20.1 kJ/mol. $\langle U_1 \rangle$ is the average potential energy per guest molecule with respect to the zeolite lattice and $RT = 2.5$ kJ/mol at 300 K. As the runs reported in Table 3 are not carried out at infinite dilution of guest molecules the CH_4–CH_4 interaction is not negligible and a direct comparison is not possible.

Of course, it would be possible to find a parameter set that reproduces all three components of the diffusion tensor and its trace (i.e., four D values) in agreement with the results obtained for the MM2 potential. At high dilution the CH_4–CH_4 interaction plays no role. Therefore, there would remain four parameters (two LJ parameters for the CH_4–Si and two for the CH_4–O interaction). This is exactly the number of D values which can be used for the fit. But, according to our feeling, such a simply mathematical fit in the four-dimensional space is rather ambiguous. Moreover, the single components of the diffusion tensor are difficult to measure [56] so, that hardly accurate values can be obtained from experiments. It is therefore unclear whether the MM2 potential yields the relative weight of the single components of the diffusion tensor correctly. The comparison in Table 3 nevertheless indicates which commonly used spherical parameters give D correctly and it shows how parameter variations influence not only the trace of the diffusion tensor but also the relative weight of its components.

6. Conclusions

The examinations show that there is an influence of the lattice and molecule vibrations on the self diffusion coefficient of methane in silicalite-1 at least for low concentrations of guest molecules. The influence of the lattice vibrations turns out to be much stronger than the influence of molecule vibrations. Both kinds of flexibility enhance the self diffusivity. As mentioned in [9] there are two effects by which lattice and molecule flexibility can influence diffusion. The additional degrees of freedom act as a heat bath (energetic effect) and the geometrical shapes of bottlenecks, potential thresholds and, may be, the molecule change periodically (geometric effect). As there are no tight bottlenecks for methane molecules diffusing within the channels of silicalite-1 the geometric effect should not be very important. So it appears to be likely that the heat bath effect supports the crossing of potential thresholds. Further investigations should clarify if the geometrical change of the threshold is also important. As the force constants of the molecule vibrations are much larger than those of the lattice vibrations the molecule is rather stiff in comparison to the lattice. A possible contribution of geometrical effects can therefore mainly be expected from lattice deformations. At high loadings the influence of the lattice vibrations and molecule vibrations as well is small. It can be seen in Fig. 8 to be within the range of fluctuations. The mutual thermalization of guest molecules is sufficient even without lattice or molecule vibrations in this case.

Effective spherical potentials were introduced for the methane–methane and the methane–lattice interaction by averaging over the orientations that appeared throughout the MD run. Evaluation of the diffusion coefficients using that model yields a rough approximation for the trace of the diffusion tensor, i.e., the over all directions averaged diffusion coefficient but bad approximations for the single components of the diffusion tensor particularly for the x-direction.

Other spherical potential models have been tested too. They show even less satisfactory results. Even a potential shown in [53] to reproduce adsorption data well does not yield good results for D. This latter finding is in agreement with the well-known fact that fitted potentials that reproduce nicely one property of a given system can fail to reproduce other properties. From the results it may be concluded that spherical potential models cannot reproduce all components of the diffusion tensor with fair accuracy.

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Appendix A. The moments of the displacement and the anisotropic diffusion tensor

The propagator for the x component is

$$P_x(x,t) = \frac{1}{\sqrt{4\pi D_x t}} \exp\left\{ \frac{-x^2}{4D_x t} \right\},$$
$$\int_{-\infty}^{\infty} \mathrm{d}x P_x(x,t) = 1. \tag{A.1}$$

Similar formulas are valid for the y and z direction.

If $D_x = D_y = D_z = D$, then the spherical symmetric propagator can be defined as

$$\begin{aligned} P(\vec{r},t) &= P_x(x,t)P_y(y,t)P_z(z,t) \\ &= (4\pi D t)^{-3/2} \exp\left\{ \frac{-r^2}{4Dt} \right\}. \end{aligned} \tag{A.2}$$

The moments of displacement yield in this case [1]:

$$\langle |\vec{r} - \vec{r}_0| \rangle = 4\sqrt{\frac{Dt}{\pi}},$$

$$\langle (\vec{r} - \vec{r}_0)^2 \rangle = 6Dt,$$

$$\langle |(\vec{r} - \vec{r}_0)^3| \rangle = \frac{32(Dt)^{3/2}}{\sqrt{\pi}},$$

$$\langle (\vec{r} - \vec{r}_0)^4 \rangle = 60(Dt)^2,$$

and D can be obtained from each one of these moments. The first moment yields

$$D = \frac{\pi}{16} \frac{\mathrm{d}}{\mathrm{d}t} \langle |\vec{r} - \vec{r}_0| \rangle^2$$

and the second moment yields

$$D = \frac{1}{6} \frac{\mathrm{d}}{\mathrm{d}t} \langle (\vec{r} - \vec{r}_0)^2 \rangle$$

and so on.

In the case of anisotropy, one can assume again that the three components of the probability distribution (propagator) are uncorrelated and hence

$$\begin{aligned} P(\vec{r},t) &= P_x(x,t)P_y(y,t)P_z(z,t) \\ &= \frac{(4\pi t)^{-3/2}}{\sqrt{D_x D_y D_z}} \exp\left\{ -\frac{x^2}{4D_x t} - \frac{y^2}{4D_y t} - \frac{z^2}{4D_z t} \right\}. \end{aligned} \tag{A.3}$$

As $r^2 = x^2 + y^2 + z^2$ is a sum of three contributions with each summand only depending on one variable, it is easy to show that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P(\vec{r},t) r^2 \,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 2D_x t + 2D_y t + 2D_z t. \tag{A.4}$$

In analogy to the spherical symmetrical case a general D can be defined by

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P(\vec{r},t) r^2 \,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z = 6Dt. \tag{A.5}$$

Because of Eq. (A.4), this D is connected with D_x, D_y and D_z by

$$D = \frac{D_x + D_y + D_z}{3}. \tag{A.6}$$

Unfortunately, such a simple procedure is not possible for the other moments as they do not consist of a sum of contributions that depend only upon one coordinate. But, the moments can be evaluated for each component. The first moment yields

$$D_x = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\pi\langle|x - x_0|\rangle^2}{4}.$$

The second moment yields

$$D_x = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\langle(x - x_0)^2\rangle}{2}.$$

The third moment yields

$$D_x = \frac{\mathrm{d}}{\mathrm{d}t}\frac{\left(\pi\left\langle|(x - x_0)|^3\right\rangle^2\right)^{1/3}}{4}.$$

The fourth moment yields

$$D_x = \frac{\mathrm{d}}{\mathrm{d}t}\sqrt{\frac{\langle(x - x_0)^4\rangle}{12}}.$$

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