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Equilibration of the kinetic energy in small zeolite cavities The thermalization effect of lattice vibrations and of mutual interaction in the diffusion of methane in a cation-free LTA zeolite

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Abstract

The guest–host and the guest–guest energy coupling in a zeolite are examined for both the vibrating and the rigid lattice. Although the effect of the vibrating lattice acting as a thermalizing heat bath is stronger than the mutual thermalization of diffusing guest molecules, as can be seen, for example, from the decay of the kinetic energy auto correlation function this mutual thermalization also leads to remarkable relaxation effects. The influence of lattice vibrations on the self-diffusion of the guest molecules is investigated. Even in the studied case of small zeolite cavities (cation-free LTA zeolite) with windows of the size of a guest molecule (methane), the influence of the lattice vibrations on the self-diffusion coefficient is negligible. Variations of interaction parameters and temperatures as well as of the elastic force constants in the lattice lead to the conclusion that the diffusion coefficient is quite stable to the influence of lattice vibrations. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zeolites; Thermalization; Energy; Relaxation; Diffusion; Transport; Ensembles

1. Introduction

Zeolites are crystals which contain a regular network of interconnected cavities [1]. They are used in many technical applications as catalysts or molecular sieves [2], a most popular application being the use as ion exchangers in phosphate-free washing agents. In connection with new technologies that save energy and protect the environment, the importance of zeolites is rapidly increasing. Because of their regular structure, zeolites are also well suited for computational investigations from which some insight can be expected even with respect to properties of other porous solids with guest molecules. The understanding of diffusion of the guest molecules is very important for many applications of zeolites since diffusion governs the reaction rate or the time constant of adsorption processes. The mechanisms of such diffusion processes can be studied well by molecular dynamics (MD) [3,4]. These computer simulations allow the detailed examination of the individual and collective properties of particle trajectories and form a well-established method for

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the investigation of diffusion processes in zeolites [2,5,6].

Because of its simple cubic structure and the missing exchangeable cations, the cation-free zeolite of type A has been chosen for several investigations e.g. Refs. [7–12]. A simple guest molecule of technical interest is methane. Methane can be expected to be approximated fairly well by a spherical Lennard-Jones particle [13].

In earlier articles about methane in silicalite it has been found that the diffusion coefficient of the guest molecules was nearly the same for the rigid and the vibrating lattice [14,15]. For the case of the cation-free A zeolite, in which the windows that connect adjacent cavities are only of the same size as the guest molecules, a strong influence of the lattice vibrations on this diffusion was found in Refs. [10,11] but, this finding was corrected in Ref. [12]. It turned out that this influence is negligible even in the case of small zeolite cavities and windows examined in [12]. Therefore, computer simulations that examine the diffusion coefficient can be done with models of the zeolite that employ a rigid lattice. In this way, on the one hand, computer time can be saved while on the other hand, the statistical error of the results can be diminished by calculating longer trajectories or including larger systems, respectively. Moreover, the potential of the guest–host interaction can easily be approximated by an analytical potential model in the case of a rigid lattice, enabling very effective simulations. This can be done by replacing the interaction site potential of the zeolite by few simple analytical functions [4,9] or by interpolating in a grid of stored potential values [16].

The long range diffusion requires passages by the guest molecules of the windows between cavities in the zeolite. Since these windows have approximately the size of methane molecules (for LTA zeolites), the self-diffusion coefficient D is very sensitive to small variations of the window diameter [8]. Therefore, it may seem to be surprising that lattice vibrations have such a small effect on D and the reason for this lack of influence should be investigated. Such a study can improve the understanding of the diffusion mechanism.

We expect two effects by which lattice vibrations may act on the diffusing particles:

The first one is the steric effect. The window size changes periodically in time due to the lattice vibration. A kind of 'breathing' can be observed. As shown in Ref. [12] (see also below), the histograms of the observed window diameters are symmetric with respect to the average values. But the question whether this symmetry leads to a vanishing effect, especially in the case of narrow windows, needs to be investigated.

The second effect is an energetic one. The vibrating lattice acts as a heat bath for the diffusing molecules. This effect can enable guest molecules to overcome potential barriers on their diffusion path. Otherwise, the diffusing molecules also act as a heat bath for each other. This mutual thermalization of the guest molecules has been examined in [7] in a simple rigid zeolite model and turned out to be very effective even at such low concentrations as $I = 1$. I is the total number of guest molecules divided by the number of cavities. The spatial particle density distribution within these MD runs agreed 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 agreed well with that of a canonical ensemble. When the mutual interaction of the guest molecules was switched off, this agreement vanished. So, the mutual interaction turned out to be the reason for the good not only overall but even local thermalization, as it had to be.

However, in Ref. [17] the relaxation time of the kinetic energy of single guest molecules was examined. Under the influence of a vibrating lattice acting as a heat bath, this relaxation time was found to be shorter than in a rigid zeolite model, where only the mutual thermalization of guest molecules was present. It was concluded that the thermalization by the lattice was stronger than the mutual thermalization of the guest molecules in the system considered in Ref. [17]. Our simulation results also confirm this conclusion (see below). This does not answer the question of how important this better thermalization is for the velocity distribution of the guest molecules or for the self-diffusion.

In this paper, the thermalization effect and the influence on D are examined in more detail in the rigid and in the vibrating zeolite lattice.

2. Method and model

As in Ref. [12], MD simulations have been carried out for the cation-free A zeolite (LTA) lattice containing 576 lattice atoms (eight cavities) in the simulation box with periodic boundary conditions. The flexible lattice is simulated using the version of the central force model of Demontis/Suffritti [18], used also in Refs. [10,11] and in Ref. [12], in which harmonic forces between the nearest neighbors in the lattice are employed. Flexibility of the angles is realized by elastic forces between oxygen atoms separated from each other by one silicon atom. Although there exist more sophisticated models [19–22], this model which is less computer time consuming has been used. If the details of the vibrational spectra are not of primary interest, the simple model is expected to supply the most important insights.

The MD cell here contains eight cavities, the number of methane molecules in our calculations is chosen to vary between 8 and 56. In other words, I varies between $I = 1$ and $I = 7$ particles per cavity on average in the runs reported here.

The trajectories have been computed using the velocity version of the Verlet algorithm [3]. The parameters used in the Lennard-Jones potentials for the guest–guest and the guest–host interaction are given in Table 1. The CH_4–O interaction is the most critical one as it determines the size of the window diameter in comparison to that of the diffusing methane molecules. For this parameter different values can be found in the literature [8]. Parameter sets A and B (see Table 1) have been introduced not only to represent the two main groups of values in the literature but also in order to examine the dependence of various effects on interaction parameters. As the self-diffusion coefficient is not very sensitive to the Lennard-Jones parameter ϵ [8], we have varied only σ, and we used $\epsilon = 0.81$ kJ/mol in this article for all simulations in sets A and B and in modifications of these parameter sets also, in order to compare the results here with those obtained in Refs. [10,11].

Table 1
Potential parameters used for simulations of CH_4 in the cation-free LTA zeolite

	σ (Å)	ϵ (kJ/mol)
CH_4–CH_4	3.817	1.232
CH_4–Si	2.14	0.29
CH_4–O (set A)	3.14	0.81
CH_4–O (set B)	3.46	0.81

The coordinates of the lattice atoms of the cation-free A zeolite are not available in the literature. Therefore, coordinates of the NaA zeolite [23] have been used in Refs. [10,11] for the rigid lattice and as initial values for the vibrating lattice. With the use of the force constants and equilibrium distances given in Ref. [18], the structure changes somewhat towards a more realistic shape during the run with the flexible lattice. The equilibrium distance (bond length) for the Si–O bond in the NaA zeolite and its cation-free analogue considered here is somewhat smaller than that for the Al–O bond in the NaA zeolite. Contrary to NaA, the cation-free LTA zeolite contains no aluminum atoms as they are replaced by silicon atoms. Therefore, only the shorter Si–O bonds appear in this zeolite.

Fig. 1(a) shows the two slightly different diameters that can be defined in the window. In Fig. 1(b), histograms of the values are given that have been obtained during an MD run for these two diameters. Values for a pure silica (cation-free) A zeolite are compared with those for a lattice containing Si as well as Al. A small but important (see Ref. [12] and Section 3) difference in the distributions of the diameters can be seen. Except for this comparison, this article deals only with the cation-free LTA zeolite.

A rigid lattice which is equivalent to the vibrating one used in Refs. [10,11] can be obtained by fixing the lattice in a state of minimal potential energy. Such a state can be realized by cooling the system during a run with the flexible lattice. Fig. 2 shows that the distributions of the two diameters resemble delta functions at a low temperature. The vertical dashed lines show the values of these diameters that would correspond to a rigid NaA

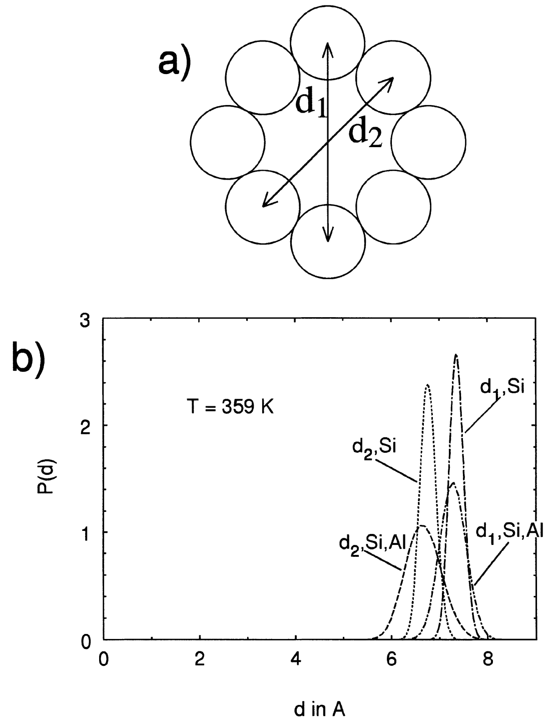

Fig. 1. (a) The definition of the two window diameters. (b) The histogram of these window diameters during a run with the flexible lattice.

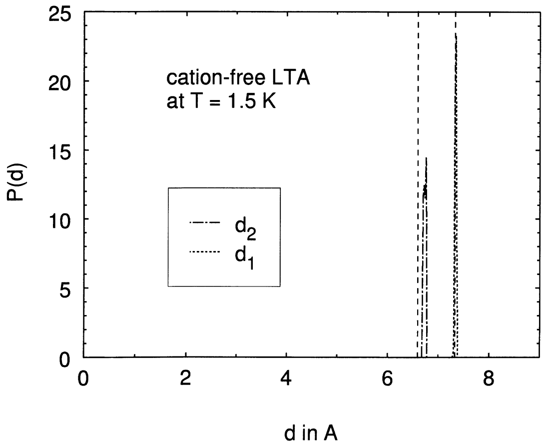

Fig. 2. Histograms for the two window diameters in the cation-free A zeolite with the flexible lattice at 1.5 K. The vertical dashed lines show the *d* values that result from coordinates from the literature for the NaA zeolite.

zeolite lattice. They are somewhat different from those of the rigid lattice produced by cooling down a vibrating cation-free LTA zeolite. If one takes into account the large sensitivity of D to a small change of the window size [8], it can be understood that this small difference turns out to be important. In fact, the influence of lattice vibrations on the self-diffusion found in Refs. [10,11] for the same system as examined in Ref. [12] and this paper was due to this slight difference (for details see Ref. [12]). Contrary to Refs. [10,11], in Ref. [12] and in this paper, the structure of the rigid lattice for the cation-free zeolite has been obtained by freezing the vibrating zeolite instead of using coordinates of the NaA zeolite.

The runs are carried out for given temperatures without perturbing the trajectories during the evaluation part of the run. This was possible by a procedure proposed in Ref. [24] and already used in Ref. [12]. The total energy that belongs to a certain temperature for a given microcanonical system can be found by a few test runs. Then, starting with an arbitrary initial value, the total energy of the MD run is adjusted to the desired value by scaling the velocities. In the simple harmonic model for the lattice vibrations, uncoupled modes are to be expected, so that the equipartition of energy may be disturbed. The fact, that the energy does not spread evenly over all degrees of freedom if only harmonic lattice vibrations are taken into account turned out not to influence the self-diffusion remarkably in some test runs in which uncoupled lattice atoms were excited artificially. The runs included a period of 10 000 steps after the adjustment of the energy in order to loose all correlations of the system to its initial artificial situation. The subsequent evaluation part of the run had a length of 5 000 000 steps and was carried out with constant total energy and momentum as a consequence of Newton's equations without external forces. The time increment per step was 10^{-15} s.

3. Results

3.1. The shape of the velocity distribution

The kinetic energy $e_{\mathrm{kin}} = p_i^2/2m$ of an arbitrarily chosen single particle i in a microcanonical ensemble of N particles and its standard deviation $\sigma_{e_{\mathrm{kin}}}$ obey to the order $1/N$ the relation

$$\frac{\sigma^2_{e_{\mathrm{kin}}}}{\langle e_{\mathrm{kin}}\rangle^2} = \frac{\left\langle \left(\frac{p_i^2}{2m}\right)^2\right\rangle - \left\langle \frac{p_i^2}{2m}\right\rangle^2}{\left\langle \frac{p_i^2}{2m}\right\rangle^2} = \frac{2}{3} - \frac{5k_{\mathrm{B}}}{3C_V} = \frac{2}{3} - \frac{5k_{\mathrm{B}}}{3Nc_V}. \qquad (1)$$

C_V is the heat capacity of the system and $c_V = C_V/N$ is the heat capacity per particle. Eq. (1) has been derived by use of a Laplace transform technique in Ref. [25] and agrees asymptotically with a similar formula derived earlier in Ref. [26]. For $N \to \infty$ the quantity defined in Eq. (1) approaches the value 2/3 which agrees with that of a canonical ensemble. In fact, it has been shown in Ref. [27] that for bulk systems of as few as 20 particles, the shape of the one particle velocity distribution in a microcanonical ensemble agrees well with that in a canonical ensemble. Since in the A zeolite at low concentrations of guest molecules these molecules are far from each other in different cages most of the time, the question arises whether our very special constraint system shows the same fluctuations in the one particle kinetic energy distribution as a microcanonical bulk system. To answer this question, six MD runs at different temperatures have been carried out for a loading of only one guest molecule per cavity, the total number of particles being therefore $N = 8$. In order to compare the results with those of Ref. [7], the CH_4–O interaction parameter σ has been chosen $\sigma_{CH_4\text{–}O} = 3.10$ Å. The Lennard-Jones parameter, $\sigma_{CH_4\text{–}O}$, must not be confused with the standard deviation $\sigma_{e_{\mathrm{kin}}}$ of the one particle kinetic energy. Five of these runs have been carried out with a rigid lattice corresponding to a microcanonical ensemble for the guest molecules. For comparison one additional run was carried out with a flexible lattice forming a heat bath for the guest molecules.

In each run, the total energy, the kinetic energy per particle e_{kin} and its variance $\sigma^2_{e_{\mathrm{kin}}}$ have been evaluated.

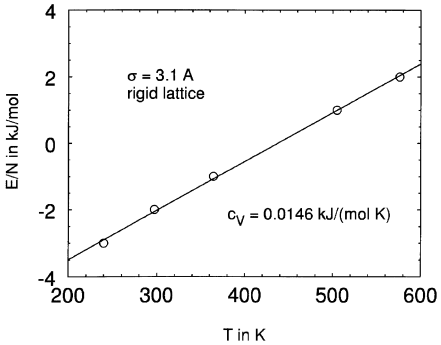

Fig. 3. The total energy per particle as a function of the temperature in runs with a rigid lattice.

$$e^{(i)}_{\mathrm{kin}} = \frac{p_i^2}{2m},$$
$$\sigma^{(i)2}_{e_{\mathrm{kin}}} = \left\langle \left(\frac{p_i^2}{2m}\right)^2\right\rangle - \left\langle \frac{p_i^2}{2m}\right\rangle^2. \qquad (2)$$

The average over all i has been taken. The heat capacity C_V can be obtained from the slope of the total energy curve in Fig. 3. The value $c_V = 0.0146$ kJ/mol K which results from these runs can be used to calculate a value for $\sigma^2_{e_{\mathrm{kin}}}/e^2_{\mathrm{kin}}$ through Eq. (1). The result is

$$\frac{\sigma^2_{e_{\mathrm{kin}}}}{e^2_{\mathrm{kin}}} = 0.548.$$

Averaging over the values of this quantity found in the first five runs shown in Table 2, one finds $\sigma^2_{e_{\mathrm{kin}}}/e^2_{\mathrm{kin}} = 0.541 \pm 0.068$ (where ± means root mean square deviation). Because of the small particle number $N = 8$, the values of $\sigma^2_{e_{\mathrm{kin}}}/e^2_{\mathrm{kin}}$ differ very much from run to run. The average value 0.541 agrees satisfactorily with the theoretical

Table 2
Runs used to evaluate the fluctuations of e_{kin}, $\sigma_{CH_4\text{–}O} = 3.1$ Å, $\epsilon_{CH_4\text{–}O} = 0.81$ kJ/mol

No.	E_{tot}/N (kJ/mol)	T (K)	$\sigma^2_{e_{\mathrm{kin}}}/\langle e_{\mathrm{kin}}\rangle^2$	Flexible
1	−3.0	240.1	0.650	No
2	−2.0	297.2	0.484	No
3	−1.0	364.4	0.505	No
4	1.0	505.0	0.563	No
5	2.0	576.1	0.502	No
6	10.47	300.7	0.684	Yes

value 0.548 from Eq. (1). This implies that, in spite of the very special nature of the system with few particles in the cavities, the fluctuations of the one particle kinetic energy follow, within the range of accuracy that could be achieved, the rules of a microcanonical ensemble. This implies that the ergodicity of the system is reached in spite of the relatively large separation of the guest molecules.

Therefore, a distribution of the one particle kinetic energy that is close to that of the canonical ensemble can be realized even for very low concentrations of guest molecules simply by increasing the number of cavities included in the same way as shown in Ref. [27] for bulk systems. If, instead of the $2^3 = 8$ cavities used in the test runs a cube of $3^3 = 27$ cavities had been used, then, for the same concentration of guest molecules with the same c_V, the value of $\sigma^2_{e_{\mathrm{kin}}}/e^2_{\mathrm{kin}}$ from Eq. (1) would be 0.632. This value is much closer to the value 2/3, which corresponds to the Maxwell–Boltzmann distribution, although 27 particles still form a very small system. In runs with a rigid lattice, the number of included cavities can be much larger than that used in Ref. [12] and in this article. Thus, e.g. in Ref. [8], runs with 343 cavities of the cation-free LTA zeolite have been carried out for the case $I = 1$. Unfortunately, such large systems cannot be employed if long range interactions like electrostatic forces require a drastically higher computational effort. But, simulations for such systems are often carried out with other compromises that make a slight deviation in the shape of the kinetic energy distribution less important. For example, the artificial periodicity of the system through the periodic boundary conditions can influence the results. If, as in Ref. [28] or with a different model in Ref. [29], these effects are avoided by use of effective short range potentials, then these approximations are also relatively crude. The steric effects of lattice vibrations could be more important if the spatial symmetry of the sites of the exchangeable cations (in a zeolite that contains such cations, not in the cation-free LTA examined here) is disturbed by lattice vibrations. This should be examined in more detail in future.

The run with the flexible lattice included in Table 2 in which the 576 vibrating lattice atoms provided a good heat bath for each guest molecule yields the value 0.684 which agrees much better with 2/3. This is in agreement with Ref. [15], where the comparison between the fluctuations of the kinetic energy in the rigid and in the vibrating lattice has been done for methane in silicalite. The remaining difference between 0.684 and 2/3 is expected to be connected with the fluctuations that appear for the small number of only eight guest molecules in the system.

3.2. Influence of lattice vibrations on D

Simulation runs with the rigid and the vibrating lattice at 300 K have been carried out for different Lennard-Jones parameters, σ, of the interaction of methane with the lattice oxygen and for loadings of $I = 1$ and $I = 7$ guest molecules per cavity. As already found in Ref. [12], Fig. 4 shows that the results for the vibrating and the rigid lattice fluctuate around each other, and no remarkable influence of the lattice vibrations can be seen. A self-diffusion coefficient D which is higher by more than one order of magnitude for a flexible lattice as found in Refs. [10,11] is in contradiction to the results shown in Fig. 4.

As mentioned in Section 1, the steric effect and the energetic effect of lattice vibrations might be thought to have influence on the self-diffusion coefficient of the guest molecules. The steric effect

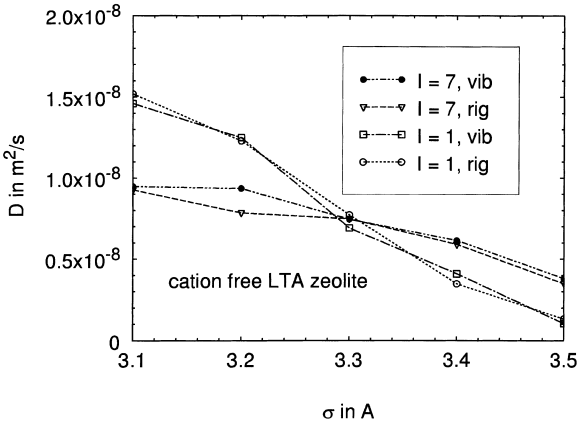

Fig. 4. The diffusion coefficient D as a function of the Lennard-Jones σ parameter of the interaction of methane with the lattice oxygen for loadings of $I = 1$ and $I = 7$ guest molecules per cavity from runs with the rigid and the vibrating lattice.

might be particularly important in the case of narrow windows (compared to the size of the guest molecule). One might predict, that in the case of a nearly closed window, the temporary opening of the window as a consequence of the vibrations is more important for the diffusion than the sometimes smaller window diameter, as the passage of a guest molecule is already unlikely for the average window size so that a further closing is unimportant. If this prediction were true, then *D* for a narrow window size should be larger in the case of a vibrating lattice.

The energetic effect is connected with the probability that a guest molecule surpasses energy barriers. The kinetic energy fluctuations that are part of the thermalization process by the lattice vibrations are expected to enhance the self-diffusion since they help the diffusing molecules to overcome potential barriers. Since a potential barrier appears in the window of the cation-free LTA in the case of a narrow window ($\sigma_{\mathrm{CH_4-O}} = 3.5$ Å) only while there is a minimum in the case of a wider window ($\sigma_{\mathrm{CH_4-O}} = 3.2$ Å), the energetic effect should also be more important in the case of the narrow window.

As the diffusion would be enhanced by both the steric and the thermalization effect, it is very unlikely that the two effects cancel each other exactly in all the different cases examined in Ref. [12] and in this article (see also below). Instead, both effects must be negligible separately.

3.3. Thermalization due to lattice vibrations and due to other guest molecules

The interesting question of the surprisingly strong mutual thermalization of the diffusants especially at low loadings found in Ref. [7] will be examined in more detail now. In Ref. [7] it was shown that the local average one particle kinetic energy is independent of the distance between the position of the particle and the cavity center. This local average is obtained by noting the kinetic energy of each particle found at a certain distance from the cavity center and taking the arithmetic mean value.

The large cavities of the A zeolites (the so-called α cages) have nearly a spherical shape. The potential energy of a single guest molecule is about −10 kJ/mol near the cavity walls i.e. at distances of about 3–4 Å from the cavity center while it is −4 kJ/mol close to the cavity center and about −15 kJ/mol in the window for the model examined in Ref. [7]. The window regions are outside of the spherical cavity at distances of more than 4.5 Å from the cavity center. As the average local kinetic energy did not depend upon the distance from the cavity center, it was concluded in Ref. [7] that this energy is also independent of the local potential energy. This corresponds to a very good thermalization. Outside of the windows but also at distances of more than 4.5 Å from the cavity center there are only regions of high potential energy forming the wall of the cavity. Therefore, in Ref. [7] the particles at distances of more than 4.5 Å were assumed to be in window regions. The few particles with high energy which sometimes penetrate into the wall have not been taken into account. This kind of evaluation has one shortcoming. The particles penetrating into the wall lose kinetic energy so that their average kinetic energy should be lower than the overall average. On the contrary, the particles entering the potential minimum that occurs in the window in this model should be accelerated. So, the average of two effects with opposite signs has been taken. To avoid this, in this work, as shown in Figs. 5 and 6, the averaging of the kinetic energy has been done for all guest molecules found with the same instantaneous

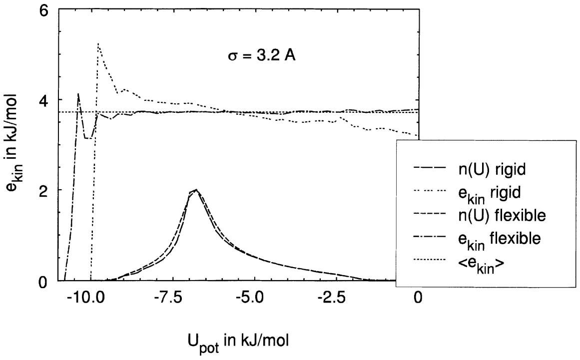

Fig. 5. Average of the kinetic energy for all guest molecules found with the same instantaneous potential energy during the run as a function of this potential energy value. $I = 1$, $\sigma = 3.2$ Å, $T = 300$ K.

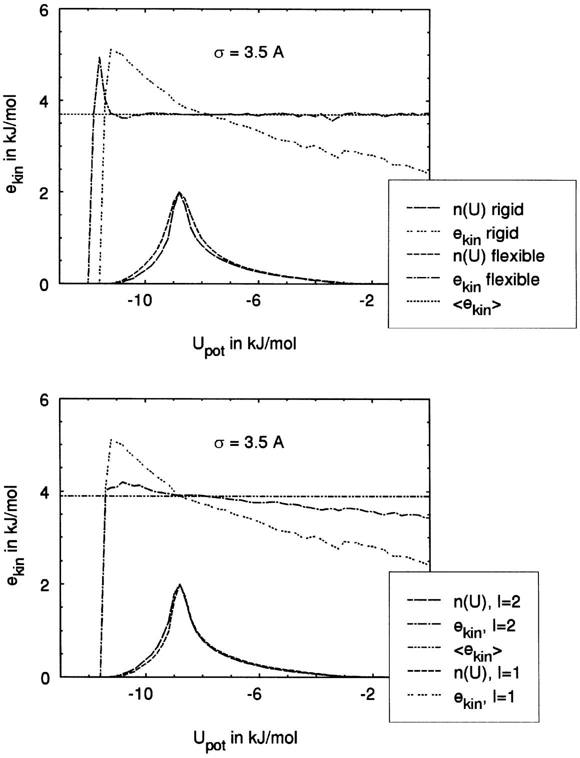

Fig. 6. Average kinetic energy of a particle as a function of its potential energy (see Fig. 5) for $\sigma = 3.5$ Å. Above $I = 1$: results for the rigid and the flexible lattice are compared. Below for the rigid lattice: results for $I = 1$ and $I = 2$ are compared.

potential energy, respectively. An average kinetic energy can be defined for each potential energy in this way. The thermalizing effect of the lattice can be compared with the mutual thermalization of the guest molecules in Fig. 5 for a loading of only one guest molecule per cavity for $\sigma = 3.2$ Å (compare to Ref. [7]). It can also be seen that, even for a rigid lattice and at low loading, larger deviations of the one particle energy from the average kinetic energy per particle occur only in regions in which the particle density is practically zero. The particle density $n(U)$, referring to the average number of particles with a value of the potential energy between U and $U + \mathrm{d}U$, is shown in arbitrary units in the lower part of the picture. In Fig. 6, the same effect is shown for $\sigma = 3.5$ Å. It turns out that the thermalization is not as good for this case. Particles that are in different cavities can exchange energy here only through long range attractive forces. This energy exchange cannot be influenced by the window diameter; a 10% change of the particle size (σ value) has negligible influence on the long range interaction. The fact that the thermalization is remarkably worse for $\sigma = 3.5$ Å indicates therefore that the more frequent inter-cavity movement of guest molecules at $\sigma = 3.2$ Å leading to more collisions plays an important role for the thermalization.

For both σ values, it can be seen that, in agreement with the corresponding finding of Ref. [17], the thermalization by the vibrating lattice is stronger than that by the mutual thermalization of the guest molecules themselves. Nevertheless, Fig. 4 shows that neither the steric effect of lattice vibrations nor the thermalizing effect of the lattice seems to have a large influence on the translational diffusion of methane.

3.4. Higher temperatures and looser lattice

In order to see whether the thermalizing effect of the lattice is more important at higher temperatures, runs have been carried out for the case $\sigma = 3.5$ Å, where the barrier in the window has a high value. This case is expected to be the most sensitive one as the barrier can disappear periodically because of the lattice vibrations. By chosing $I = 1$ the mutual thermalization of the guest molecules is chosen to be small. Fig. 7 shows that even

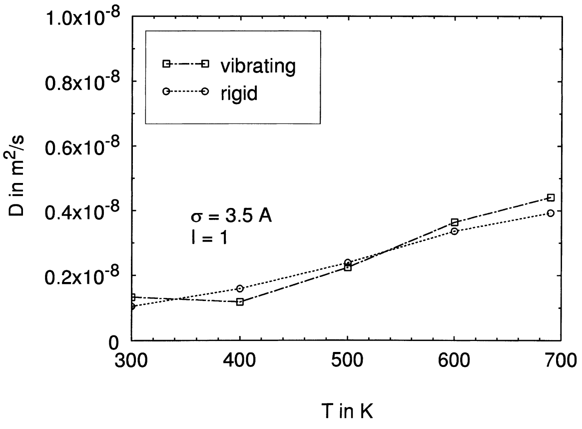

Fig. 7. D as a function of the temperature for $\sigma = 3.5$ Å.

in this case no influence of the lattice vibrations on the diffusion can be seen for temperatures up to 690 K.

Additional runs with the vibrating lattice have been carried out, in which the force constants had lower values k/f instead of k with $f > 1$ for the case $I = 1$, $\sigma = 3.5$ Å. As pointed out in Refs. [10,11], the Fourier transform of the guest particle motion overlaps with the spectrum of the lattice vibrations only in a small region of high frequencies that corresponds to low frequency modes of the lattice vibrations. Therefore, a stronger energy exchange can be expected if the force constants of the lattice are lower leading to lower frequencies for the lattice vibrations. Fig. 8(a) shows the histograms of the two window diameters for the loosest lattice examined here compared with the original ones. It can be seen that the fluctuations of these diameters for the loose lattice are larger but still much smaller than the average values of the diameters. The diminished force constants cause larger amplitudes in the lattice vibrations as well as lower frequencies for the lattice vibrations. The latter should lead to a stronger coupling between the translational motion of the guest molecules and the lattice vibrations. So, both of the possible reasons for an influence of the lattice vibrations on the diffusion of the guest molecules namely the steric effect and the energetic one should increase if the force constants in the lattice have lower values. In Fig. 8(b) an influence of the lattice vibrations on the diffusion in the direction as forecasted in Refs. [10,11] can be seen, but it is of lower magnitude than it was found there and it only appears for very loose lattices. Moreover, the last values in this curve are not very accurate as the root mean square deviation of the D values turned out to increase strongly with lower force constant values. Since one run did not seem to yield an acceptable accuracy for $f = 10$, five runs have been carried out. The D values from these runs are 2.41×10^{-9}, 1.70×10^{-9}, 1.59×10^{-8}, 1.78×10^{-9} and 4.00×10^{-9} m^2/s, respectively. The D value 5.16×10^{-9} m^2/s for $f = 10$ in Fig. 8(b) is the arithmetic average of these five results. The root mean square deviation is 6×10^{-9} m^2/s in this extreme case. So, this last value is not very reliable.

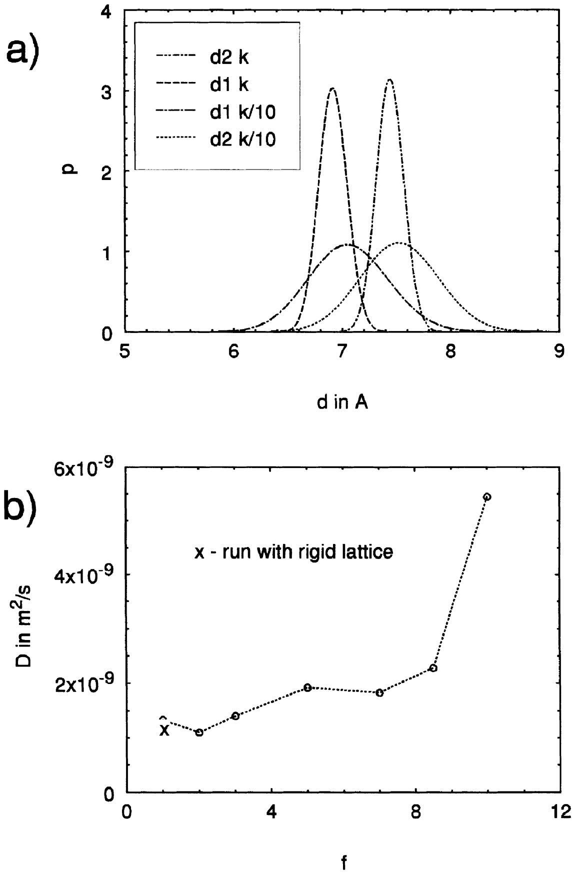

Fig. 8. Results from runs with force constants k/f instead of k: (a) Histograms of the window diameters defined in Fig. 1(a) for the original and the reduced force constants with $f = 10$. (b) D from runs with different f values. The cross marks the run with rigid lattice for comparison.

4. The auto-correlation function of the kinetic energy

A quantity that is sensitive to the presence of a rigid or flexible wall is the change of the kinetic energy of the single particle e_{kin} during collisions with the wall. Therefore, the auto-correlation function (ACF) $G(t')$ of the fluctuations $\Delta e_{\mathrm{kin}}(t)$ of this energy has been examined. This quantity is defined by

$$\Delta e_{\mathrm{kin}}(t) = e_{\mathrm{kin}}(t) - \langle e_{\mathrm{kin}} \rangle, \tag{3}$$

where $\langle e_{\text{kin}} \rangle$ is the average kinetic energy of a particle. The ACF is defined as

$$G(t') = \frac{\langle (e_{\text{kin}}(t+t') - \langle e_{\text{kin}} \rangle)(e_{\text{kin}}(t) - \langle e_{\text{kin}} \rangle) \rangle}{\left\langle (e_{\text{kin}}(t) - \langle e_{\text{kin}} \rangle)^2 \right\rangle}. \tag{4}$$

for both the rigid and the flexible lattice. Figs. 9 and 10 show the different ACFs obtained for the rigid and the flexible lattice and for a wide ($\sigma = 3.1$ Å) and for a narrow ($\sigma = 3.5$ Å) window, respectively. For each window size the correlations to the prior values are lost faster if the lattice is flexible. This is expected as, in collisions of a guest molecule with a flexible wall, energy is exchanged while, in collisions of a particle with a rigid wall, the wall neither takes energy from nor gives energy to the particle.

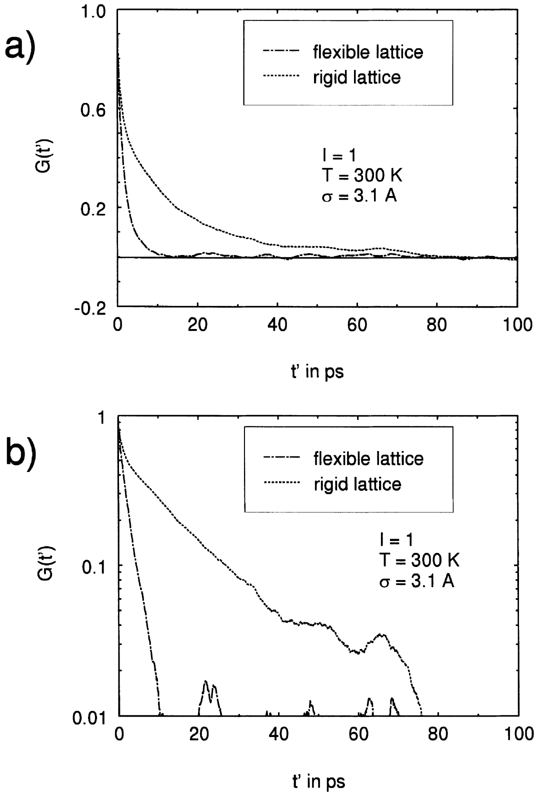

Fig. 9. ACF of Δe_{kin} for a single particle in the case $\sigma = 3.1$ Å: (a) linear coordinate axes; (b) with a logarithmic scale for the ACF axis.

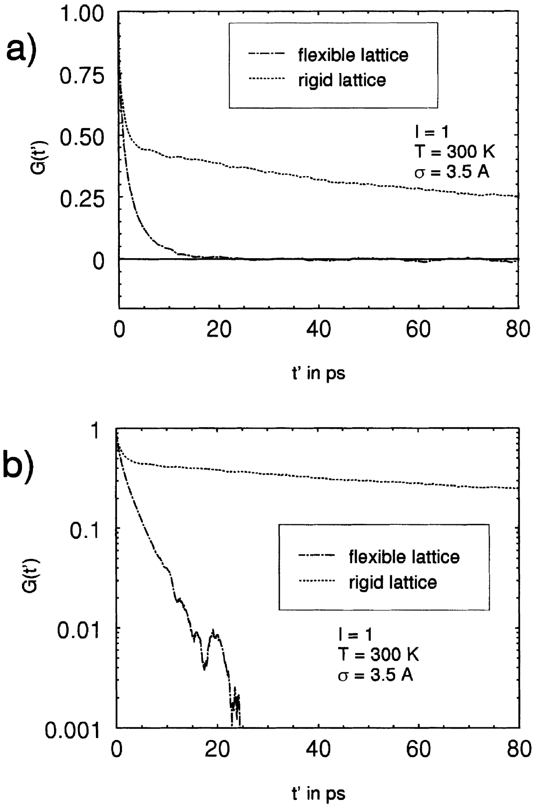

Fig. 10. The same as in Fig. 9 but for $\sigma = 3.5$ Å.

The quantity $G(t')$ defined in Eq. (4) depends only upon the time difference t' but not upon t in the stationary state. Therefore, an average over all t has been carried out. In order to characterize the decay of the ACF quantitatively a relaxation time τ can be defined for those time intervals, where the decay is an approximately exponential one.

Let t_1 and t_2 be the limits of such a time interval, where $\ln G(t')$ shows a linear time dependence. For $\sigma = 3.1$ Å, Fig. 9(a) shows that for the rigid lattice $t_1 \approx 5$ ps and $t_2 \approx 30$ ps. Then G fulfills approximately the relation

$$G(t_2) = G(t_1) \exp\left\{ \frac{t_1 - t_2}{\tau} \right\} \tag{5}$$

from which

$$\tau = \frac{t_1 - t_2}{\ln\left\{ \frac{G(t_2)}{G(t_1)} \right\}} \tag{6}$$

Table 3
Relaxation times τ in ps for the decay of the function $G(t')$

σ (Å)	Rigid lattice	Flexible lattice
3.1	16.3	2.22
3.5	142.7	3.10

can be obtained. The relaxation times τ found in this way are listed in Table 3.

It is interesting that τ for the rigid lattice is much longer in the case of the narrow window than for the wide window. As collisions with the wall do not change the energy of the individual guest molecules, the mutual energy exchange between the guest molecules must be larger in the case of a wider window. This result again confirms the finding that, for the mutual thermalization of guest molecules, window passages i.e. diffusion plays an important role.

5. Conclusions

In agreement with the results published in Ref. [8], the self-diffusion coefficient is strongly influenced by a small change of the average window diameters. Therefore, the small difference in the zeolite structure between the models employed for the rigid zeolite in Refs. [10,11] on the one hand and [12] and this paper on the other hand leads to dramatically different results.

On the contrary, negligible influence of lattice vibrations on D is found if equivalent lattices are used for the runs with the rigid and the vibrating lattice. A rigid lattice equivalent to the vibrating one is reached simply by cooling down the vibrating lattice in order to find a structure for the rigid lattice by potential energy minimization. The missing effect of the lattice vibrations on the diffusion of guest molecules leads to the conclusion that the mutual thermalization of the guest molecules is sufficient for the passage of the potential barrier and that the deviation of the shape of the velocity distribution from the Maxwell–Boltzmann distribution is not important for D. The steric effect of the vibrations on the window size may be of small influence since it is a symmetrical one. It leads not only to instantaneous lower but with the same frequency to instantaneous higher potential thresholds.

The value of D is not changed by lattice vibrations over a large range of temperatures. Even with smaller force constants and therefore larger oscillations of the window diameters and probably a stronger energetic coupling between the guest molecules and the lattice, D is not changed by lattice vibrations if all force constants are divided by a parameter f with $1 \leqslant f \leqslant 3$. If f is greater than 5, then the self-diffusion coefficient D is larger for the case of a vibrating lattice. So, at least the tendency of the effect predicted in Refs. [10,11] is correct.

The mutual thermalization of the guest molecules investigated in Ref. [7] in a rigid zeolite lattice is not sufficient to lead to a total equilibration of the kinetic energy of the individual guest molecules at all times and at all sites within the cavity. The more detailed examinations in this article and the comparison with the runs in the vibrating lattice show, in agreement with Ref. [17], that the thermalizing effect of the vibrating lattice on guest molecules is stronger than their mutual thermalization at low loadings. Nevertheless, larger deviations of the average local kinetic energy appear only in regions in the zeolite, where the probability of finding guest molecules is relatively small. Moreover, the agreement of D values for the rigid and the vibrating lattices shows that the steric effect of oscillations of the window size and the additional thermalization of the guest molecules by the vibrating lattice leave D unchanged.

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References

[1] D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, 1974.

[2] H. Chon, S.-K. Ihm, Y.S. Uh (Eds.), Progress in Zeolite and Microporous Materials, Studies in Surface Science and Catalysis, vol. 105, Elsevier, Amsterdam, 1997.

[3] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Clarendon, Oxford, 1989.

[4] R. Haberlandt, S. Fritzsche, G. Peinel, K. Heinzinger, Molekulardynamik – Grundlagen und Anwendungen, including a chapter about Monte-Carlo-simulations, written by H.-L. Vörtler, Vieweg, Wiesbaden, 1995.

[5] D.N. Theodorou, R.Q. Snurr, A.T. Bell, Molecular dynamics and diffusion in microporous materials, in: G. Alberti, T. Bein (Eds.), Comprehensive Supramolecular Chemistry, vol. 7, Pergamon, Oxford, 1996, pp. 507–548.

[6] P. Demontis, G.B. Suffritti, Chem. Rev. 97 (1997) 2845.

[7] S. Fritzsche, R. Haberlandt, J. Kärger, H. Pfeifer, M. Wolfsberg, Chem. Phys. Lett. 171 (1990) 109.

[8] S. Fritzsche, R. Haberlandt, J. Kärger, H. Pfeifer, K. Heinzinger, Chem. Phys. 174 (1993) 229.

[9] S. Fritzsche, Phase Transitions 52 (1994) 169.

[10] P. Demontis, G.B. Suffritti, Chem. Phys. Lett. 223 (1994) 355.

[11] P. Demontis, G.B. Suffritti, Molecular dynamics simulations of diffusion in a cubic symmetry zeolite, in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Hoelderich (Eds.), Proceedings of the Tenth International Zeolite Conference, Elsevier, Amsterdam, 1994, pp. 2107–2113.

[12] S. Fritzsche, M. Wolfsberg, R. Haberlandt, P. Demontis, G.B. Suffritti, A. Tillocca, Chem. Phys. Lett. 296 (1998) 253.

[13] M. Schoen, C. Hoheisel, O. Beyer, Mol. Phys. 58 (1986) 699.

[14] P. Demontis, E.S. Fois, G.B. Suffritti, S. Quartieri, J. Phys. Chem. 94 (1990) 4329.

[15] P. Demontis, G.B. Suffritti, E.S. Fois, S. Quartieri, J. Phys. Chem. 96 (1992) 1482.

[16] P.L. June, A.T. Bell, D.N. Theodorou, J. Phys. Chem. 94 (1990) 8232.

[17] G. Schrimpf, M. Schlenkrich, J. Brickmann, B. Bopp, J. Phys. Chem. 96 (1992) 7404.

[18] P. Demontis, G.B. Suffritti, S. Quartieri, E.S. Fois, A. Gamba, J. Phys. Chem. 92 (1988) 867.

[19] P. Demontis, G.B. Suffritti, S. Quartieri, E.S. Fois, A. Gamba, Zeolites 7 (1987) 522.

[20] C.R.A. Catlow, M.C. Freeman, B. Vessal, S.M. Tomlinson, M. Leslie, J. Chem. Soc. Faraday 87 (1991) 1947.

[21] P. Demontis, G.B. Suffritti, S. Bordiga, R. Buzzoni, J. Chem. Soc. Faraday 91 (1995) 525.

[22] V.A. Ermoshin, K.S. Smirnov, D. Bougeard, J. Mol. Struct. 410 (1997) 371.

[23] W.M. Meier, D.H. Olson, Atlas of Zeolite Structure Types, Butterworths, London, 1992.

[24] S. Fritzsche, Habilitationsschrift, Leipzig, 1999.

[25] E.M. Pearson, T. Halicioglu, W.A. Tiller, Phys. Rev. A32 (1985) 3030.

[26] J.L. Lebowitz, J.K. Percus, L. Verlet, Phys. Rev. 153 (1967) 250.

[27] J.R. Ray, H.W. Graben, Phys. Rev. 44A (1991) 6905.

[28] S. Fritzsche, R. Haberlandt, J. Kärger, H. Pfeifer, K. Heinzinger, M. Wolfsberg, Chem. Phys. Lett. 242 (1995) 361.

[29] P. Demontis, G.B. Suffritti, Mol. Phys. 91 (1997) 669.