6 November 1998

Chemical Physics Letters 296 (1998) 253–258

CHEMICAL PHYSICS LETTERS

About the influence of lattice vibrations on the diffusion of methane in a cation-free LTA zeolite

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Received 7 August 1998

Dedicated to Prof. Dr. Dr. H. Pfeifer on the occasion of his 70th birthday

Abstract

The influence of lattice vibrations on the diffusion of methane in a cation-free zeolite of structure Type LTA is examined. It is shown that contrary to earlier published results the self-diffusion coefficients obtained with flexible and with rigid lattices are practically the same. This finding is true over a wide range of temperatures and for different interaction parameters. The reason why earlier papers did not state this independence of D on the lattice vibrations is explained. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

There is an increasing interest in zeolites, not only because of their technical applications but also due to their interesting properties with respect to adsorption and migration of guest molecules [1]. The most important features of these microporous crystals for industrial purposes are ion exchange, molecular sieving and shape-selecting catalytic properties. The great variety of transport properties of guest molecules in zeolites makes them an interesting object of scientific studies [2]. Computer simulations form a particularly well suited tool for gaining insight into details of such transport mechanisms. Therefore, they are extensively used in this field [1].

Many simulations reported in the literature examine the behaviour of guest molecules in zeolites using the approximation of a rigid lattice in order to enable higher statistical accuracy or the treatment of more complex systems. The examination of diffusion requires particularly long trajectories so that the computational effort severely limits the statistical accuracy of the results and simplifications are welcome. The reliability of such simulations, however, must be checked carefully. For example, the particle density and energy distribution within the cavity are important for the diffusion of guest molecules in zeolites since the diffusing particles have to pass regions of different potential energy. Energy transfer to particles approaching a potential barrier can be

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PII: S0009-2614(98)01060-4

decisive for the possibility of passing this barrier. The assumption of a rigid lattice is without doubt only an approximation and cannot be adequate for all purposes. It has turned out, however, that important properties of the real system can be found using this approximation [3]. Even at concentrations of methane as low as one guest molecule per cavity $(I = 1)$ in the so called cation-free LTA (i.e free of exchangeable cations outside the lattice) zeolite, the density distribution in the cavity was the same for molecular dynamics (MD) simulations with the rigid lattice and for Metropolis Monte Carlo sampling which corresponds to ideal thermalization. Furthermore, the local average kinetic energy of single particles was nearly independent of the distance from the cavity center, even at $I = 1$. This local average kinetic energy is defined as the instantaneous kinetic energy of particles found at a given site averaged over many observations. The density distribution and the local kinetic energy found in MD changed drastically when the mutual interaction between guest molecules was switched off. Therefore, in the simulations reported before, with guest–guest interaction and a rigid lattice, this mutual interaction must be the reason for the satisfactory local energy and particle distribution.

Another important property of the system is the shape of the kinetic energy probability distribution. It is well known that the fluctuations of the kinetic energy of the simulated system [4] and that of a single particle [5] are smaller in a microcanonical ensemble of a few particles than in a canonical ensemble. Tests in MD simulations with the rigid lattice confirmed this finding [3,6,7]. Nevertheless, the one particle velocity distribution approaches that of a canonical ensemble with increasing particle number. In [5] it has been shown that for a bulk system of 20 particles the one particle velocity distribution already nearly perfectly agrees with the Maxwell–Boltzmann distribution. In simulations with the rigid lattice it is not problematic to include many cavities in the simulated system (e.g., 343 cavities of the cation-free LTA zeolite in [8] for the case $I = 1$). In Ref. [9] it has been shown that the width of the one particle kinetic energy distribution of guest molecules in the rigid zeolite lattice converges to that of the canonical ensemble with increasing N according to the same law as in a microcanonical bulk fluid. Therefore, the difficulty of the narrower velocity distribution in the rigid lattice case can easily be avoided by increasing the system size in order to include 20 or more guest molecules, even in the case of the occupation number $I = 1$.

In addition to the stationary distributions of density and energy, the time scale in the thermalization of the moving molecules may be important. It was found that kinetic energy relaxations caused by the lattice as a heat bath had smaller relaxation times than those caused only by the mutual thermalization of guest molecules [10] and that the thermalization in regions where guest molecules seldom appear is much better in the vibrating zeolite at the low occupation number of one guest molecule per cavity [9]. The question as to whether this difference between systems with rigid and flexible lattice influences the self-diffusion coefficient D_S will be checked in this Letter by comparison of D_S values.

Another effect connected with lattice vibrations which may influence the diffusion of guest molecules is the steric effect of the periodic oscillations of the window size. The passages through the windows by the guest molecules is decisive for long range diffusion. Particularly, in the case of narrow or almost closed windows, the question as to whether the temporary opening of the windows leads to more frequent passages can be answered if the D_S values from the runs with the rigid lattice are compared with those from the vibrating lattice.

In Refs. [6,7], a large influence of lattice vibrations on the diffusion coefficient of methane in a cation-free LTA zeolite was reported. More detailed examinations in the present Letter lead to a modification of this result. Additionally, such examinations can give interesting insights into the mechanisms of diffusional motion. The influence of lattice vibrations on the transport of guest molecules may also be interesting with respect to the design of new artificial zeolitic materials for industrial purposes, since the transport of guest molecules is important in most applications. Therefore, it is of interest to find out if the flexibility of the lattice is important.

2. Details of the simulations

In Ref. [8] the self-diffusion of guest molecules has been examined for two different sets (A and B) of interaction parameters (Table 1). The interrela-

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

	σ in Å	ϵ in kJ/mol
CH_4–CH_4	3.817	1.232
CH_4–Si	2.14	0.29
CH_4–O (set A)	3.14	1.5
CH_4–O (set B)	3.46	0.81

tions between small geometrical changes in the lattice and transport properties can be examined in this way. Furthermore, different potential parameters are used in the literature for the CH_4–O interaction by different authors [8].

The most important parameter is the Lennard–Jones parameter σ for the CH_4–O interaction which is decisive for the size of the window connecting adjacent cavities. Since the self-diffusion coefficient D_S strongly depends on this window size a large influence of the lattice vibrations on D_S could be expected, but this is not the case, as shown below.

For the vibrating lattice, the simple harmonic central force model [11] (which was used in Refs. [6,7] also) has been employed. Although more sophisticated models exist [11–14] the less computer-time consuming model has been used. If the details of the vibrational spectra are not of primary interest, the simple model reproduces the lattice vibrations well enough.

The structure of the zeolite lattice as well as the edge length of 24.55 Å for the basic crystallographic unit, which is also the simulation box, have been taken from [15]. Eight cavities formed the MD box. Thus, the runs have been performed with 576 lattice atoms and with either 8 or 56 ($I = 1$ or 7) diffusing methane molecules.

The temperature was adjusted by the procedure proposed in Ref. [9]. In this procedure, the total energy of the simulated system corresponding to a selected temperature is determined by test calculations. It is then easy to adjust the total energy of the MD run to this value by scaling the velocities. The fact that the energy does not spread perfectly over all atoms in the lattice if only harmonic lattice vibrations are taken into account turned out not to influence D_S remarkably in some test runs in which uncoupled lattice atoms were excited artificially. After the adjustment of the total energy a short run of 10 000 steps allowed the system to equilibrate. During this period, and during the following evaluation part of the run, the evolution of the system was governed by Newtons laws only without being disturbed from outside. The evaluation part was 5 000 000 steps long for each run. The time step was 10^{-15} s.

Fig. 1 shows the two slightly different window diameters which can be found from the ring of oxygen atoms forming the window in a cation-free LTA zeolite. Fig. 2 shows histograms for these two diameters obtained during MD runs with a flexible lattice In graph (a) such histograms at 360 K for two different zeolites are compared. One is the cation-free LTA. The lattice contains only silicon atoms besides the oxygen. The other one is an A zeolite with Si/Al ratio 1:1 (e.g. the NaCaA zeolite in which all windows are open). The diffusion in this zeolite is not examined in this Letter. It has been introduced here only in order to illustrate different binding lengths that appear in the two types of lattice. The additional exchangeable cations which are present in Al containing A zeolites are neglected. They are not part of the lattice but they are only kept at the cavity wall by electrostatic attraction. Thus, they will have low influence on the window fluctuations in those zeolites (e.g. the NaCaA zeolite) where they are not on positions inside the window.

From Fig. 2 it can be seen that the average window diameter is somewhat smaller in the case of

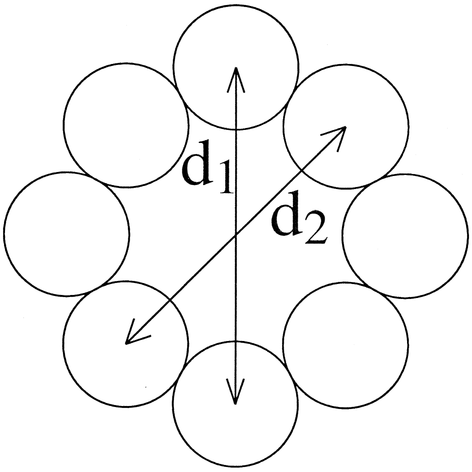

Fig. 1. The two window diameters.

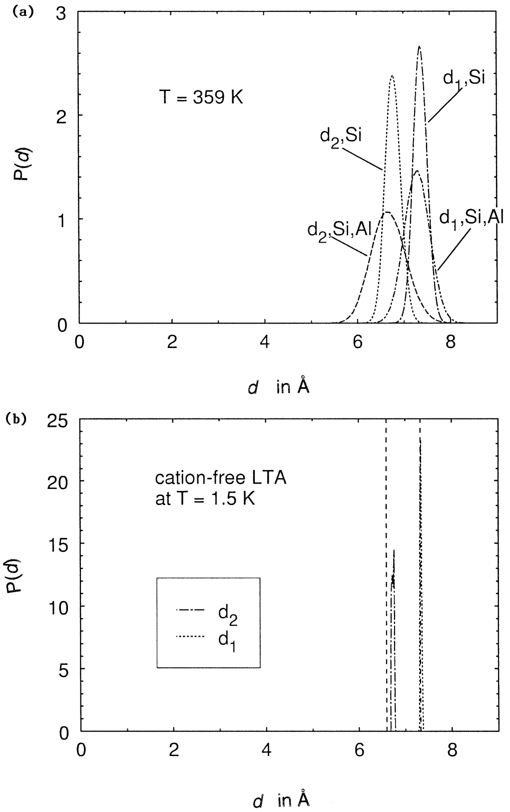

Fig. 2. Histograms for the two window diameters. (a) comparison of the histograms for the A zeolite containing Si, Al (and exchangeable cations) and the cation-free pure Si zeolite A; at 360 K. (b) the same histograms for the pure silica zeolite at 1.5 K. The vertical dashed lines show the *d* values from the literature (NaA–zeolite).

the A zeolite which contains also Al atoms and the fluctuations are larger. Therefore, the positions of lattice atoms must be different for the two types of zeolites. Unfortunately, until now only positions for the cation containing A zeolite could be found in the literature. In [6,7] and in the present Letter these coordinates are used as starting positions for runs with the vibrating lattice for the cation-free LTA zeolite too. Since the correct bond length and realistic force constants are employed for the elastic bonds, the lattice approaches the correct geometry during the thermalization part of the run. Thus, different window sizes can be observed in Fig. 2 for different Si:Al ratios in the lattice respectively.

The coordinates for simulations with the rigid lattice for the cation-free LTA zeolite cannot be taken from the literature if comparison with results from runs with the flexible lattice are carried out. Instead, an equivalent lattice for the rigid cation-free zeolite can be obtained from a run with a vibrating lattice by cooling the system down to absolute zero temperature thus yielding a potential energy minimization. In the lower graph in Fig. 2, the histograms of the two window diameters can be seen for the cation-free zeolite at a temperature of 1.5 K. The positions are almost rigidly fixed at this temperature. For comparison, vertical dashed lines show the *d*-values $d_1 = 7.3$ Å and $d_2 = 6.6$ Å used for the fixed framework simulations reported in Refs. [6,7]. They correspond to the experimental coordinates obtained by Pluth and Smith for the NaA zeolite [16]. It appears that the value of the smaller, and crucial, diameter d_2 is lower for the NaA than for the cation-free LTA.

3. Results

Runs with vibrating and with rigid cation-free LTA lattices have been carried out. Contrary to [6,7], the sites of the lattice atoms for the runs with a rigid lattice have been obtained by the energy minimization which was mentioned above.

In Fig. 3, no influence of the lattice vibrations on the self-diffusion of methane can be seen. The influence of the lattice vibrations on this diffusion found in Refs. [6,7] was due to the slight difference in the lattices used for runs with rigid and vibrating lattices, respectively. Indeed, for the fixed framework simulations in Refs. [6,7] the experimental coordinates of the fully aluminated zeolite NaA [16] were assumed. As Al–O bond distances are about 1.76 Å, compared with 1.60 Å for the Si–O bond distances and the cell dimensions were the same, the window diameter was smaller (by about 0.3 Å) than the corresponding average value of the all–silica framework which was used for the vibrating framework simulations, as shown in Fig. 2. Therefore, the difference between the two situations was abnormally emphasized. On the other hand, from the results reported in Fig. 3, where the diffusion coefficients obtained by changing the sorbate diameter are shown, it may clearly be seen that the sensitivity of the diffusion coefficients to small variations of the relative dimensions of the

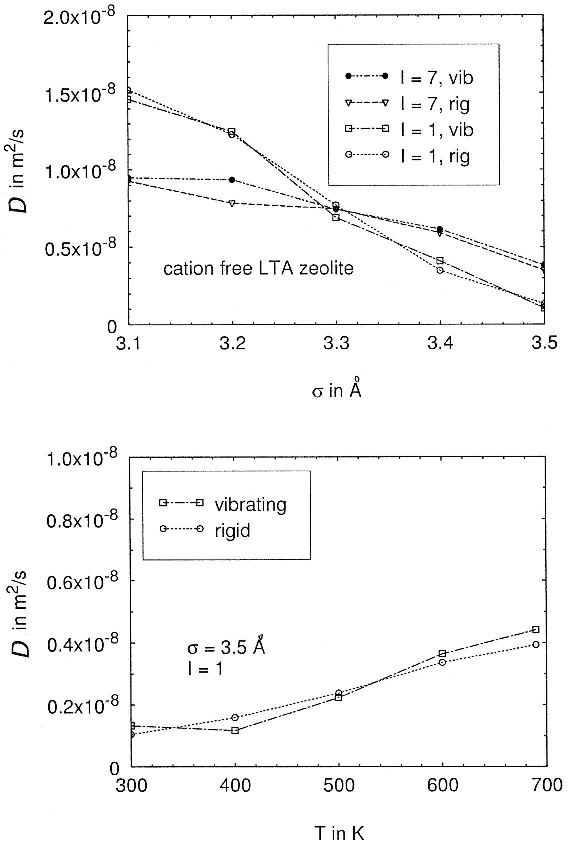

Fig. 3. Above: The diffusion Coefficient D as a function of the Lennard–Jones σ parameter of the interaction of methane with the lattice oxygen for loadings of $I = 1$ and $I = 7$ guest molecules per cavity from runs with rigid and vibrating lattices at $T = 300$ K. Below: D as function of the temperature for $\sigma = 3.5$ Å.

window and of the sorbate molecule is apparent, especially for low loadings.

In order to see whether the effect of the lattice vibrations on diffusion is more important at higher temperatures, runs for the case $\sigma_{\mathrm{CH4-O}} = 3.5$ Å have been carried out. For such large values of $\sigma_{\mathrm{CH4-O}}$ the windows are nearly closed and a potential barrier appears in the window. Therefore, D_S in this case is expected to be more sensitive to lattice vibrations than in other cases. Additionally, by choosing $I = 1$ the mutual thermalization of the guest molecules is chosen to be small. Fig. 3 shows, however, that even in this case – for temperatures up to 690 K – no influence of lattice vibrations on the diffusion can be seen.

4. Conclusions

The lack of 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. The reason why the steric effect of the ‘breathing’ window has a small influence is perhaps the symmetrical nature of this steric effect. It leads not only to instantaneous lower but, also with the same probability, to instantaneous higher potential barriers.

For fast processes taking place in the cavity, e.g. relaxations [10,17] or chemical reactions [18,19], the influence of lattice vibrations cannot be neglected.

Acknowledgements

The authors thank Prof. J. Kärger and Prof. D.N. Theodorou for stimulating discussions and the SFB 294 for financial support. RH also thanks the Fonds der chemischen Industrie for financial support.

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