

MD — Simulation of Diffusion of Methane in Zeolites of Type LTA

Siegfried Fritzsche, Martin Gaub, Reinhold Haberlandt*, Gerd Hofmann

Universität Leipzig, Fakultät für Physik und Geowissenschaften, Institut für Theoretische Physik, Augustusplatz 10-11, D-04109 Leipzig, Germany (sfri@sunstat1.exphysik.uni-leipzig.de)

Received: 15 May 1996 / Accepted: 6 August 1996 / Published: 27 September 1996

Abstract

Using molecular dynamical computer simulations (MD) the dynamics of kinetic processes in zeolites will be discussed on a molecular level. Small changes in lattice parameters can cause dramatical changes in the diffusion coefficient. The presence of cations Na^+ , Ca^{2+} also strongly influences the diffusion. Changes of the self-diffusivities will be discussed that appear if a vibrating lattice instead of a rigid one is used. Nonequilibrium simulations show the correlation between transport-diffusion and self-diffusion in zeolites.

Keywords: MD, zeolites, diffusion processes

Introduction

The study of diffusion processes in zeolites is of great interest because these crystals contain very regular internal surfaces and they are used for many industrial purposes [1]. Molecular dynamical computer simulations (MD) [2, 3] that give insight in the dynamics of kinetic processes in zeolites will be discussed on a molecular level. Furthermore, MD allows variations in the system parameters that are not possible in experiments. Starting from late eighties interrelations and dependencies have been examined by MD [4 – 14].

Simulations

The MD simulations were carried out using the velocity-Verlet-algorithm [2, 3] with up to 6,000,000 time steps of 5 and 10 fs, respectively. The basic MD box contains 8 up to 343 large cavities with occupation numbers varying between 1 and 11 per cavity, respectively.

For the interaction between the guest molecules CH_4 and the lattice atoms we use a Lennard-Jones (LJ) (12,6) potential

$$U(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} \quad (1)$$

with ϵ as the minimum depth of the potential energy and σ defined by $U(\sigma) = 0$, respectively. For NaCaA additional polarization energy terms due to the cations have been included. Using the conventional microcanonical MD ensemble the self-diffusivity is calculated while a more generalized non-equilibrium (NEMD) ensemble is used to determine the transport-diffusivities.

Figure 1 shows the general structure of zeolites of type LTA used for our calculations. The sodalite units form a cubic lattice with large cavities connected by so-called 'windows' consisting of eight oxygen atoms.

In figure 2 the distribution of the lattice atoms around a large cavity in the NaCaA zeolite is to be seen. Lattice atoms

* To whom correspondence should be addressed

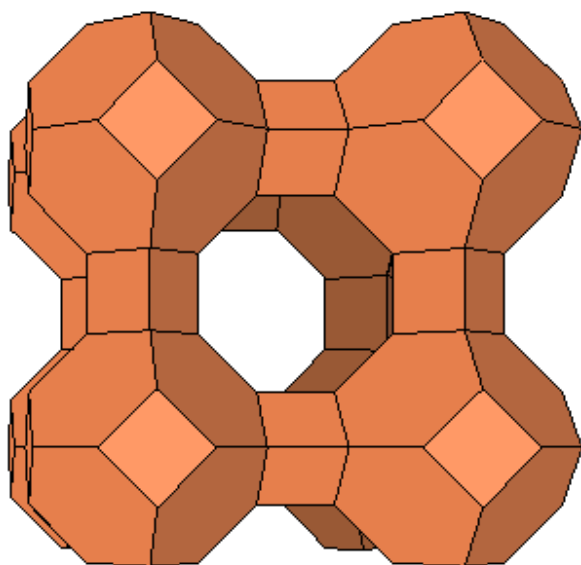


Figure 1. General structure of zeolites of type LTA

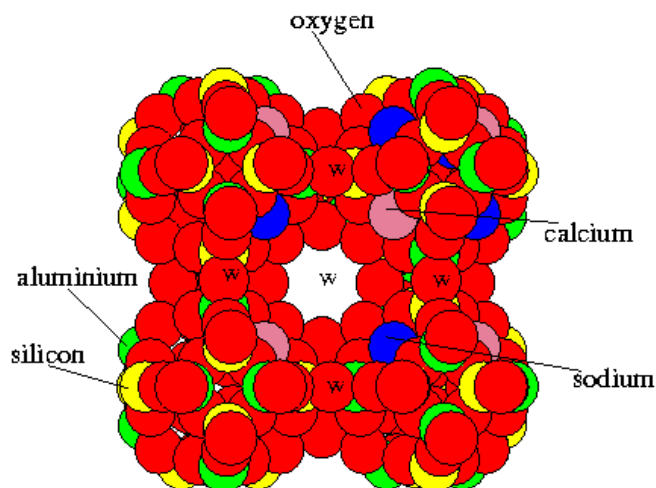


Figure 2. View into a NaCaA - zeolite

in front have been removed in order to see the interior of the cavity. Windows are marked by a small w.

Results

Residence times and velocity-auto-correlation functions (vacf)

We define the residence time for a given guest molecule as the time difference between subsequent passages of limiting planes. Such a plane is situated in the center of each window perpendicular to the window axis.

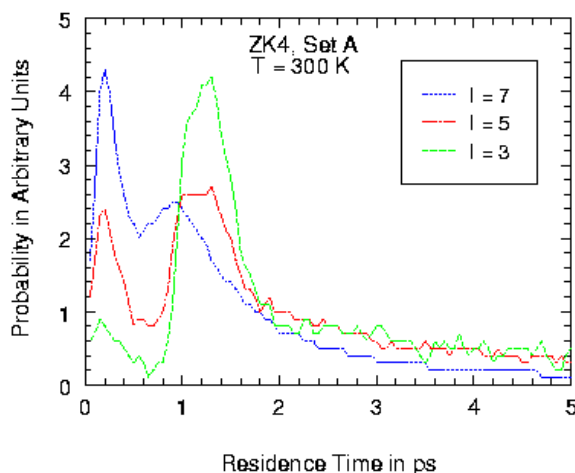


Figure 3. Histogram of the residence time for different concentrations of guest molecules

Figure 3 shows the probability density of the thus defined ‘residence times’ within the individual cavities for three different sorbate concentrations (model A). The first maximum at ~ 0.3 ps corresponds to times which are too short to allow a passage through the cavity to one of the five other windows [8]. Therefore, this maximum must be attributed to trajectories, which are reversed immediately after the molecule has passed the window. It is interesting to note that the intensity of this first maximum increases with increasing sorbate concentration. It may be concluded, therefore, that the reversal in the trajectory is mainly caused by the influence of the other adsorbate molecules. These conclusions are confirmed by minima in the velocity-auto-correlation function (vacf) (see [8]) where the time and the density dependence of these minima are in agreement with the reasoning above.

Propagator

The propagator is defined as the conditional probability density to find a particle at time t at the place $\vec{r}_0 + \vec{r}$ if it has been at time $t = 0$ at \vec{r}_0 . For a pure random walk the propagator is a Gaussian distribution

$$P(\vec{r}, t) = (4\pi Dt)^{-\frac{3}{2}} \exp\left\{-\frac{r^2}{4Dt}\right\} \tag{2}$$

Figure 4 shows the propagator for zeolites with structural effects in correspondence to the structure of the zeolite

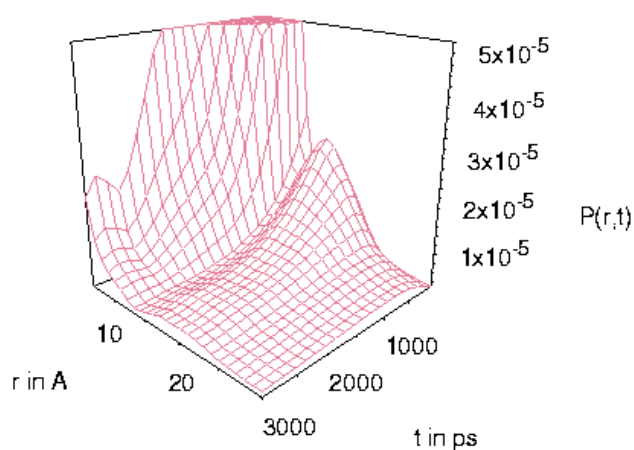


Figure 4. Propagator $P(\vec{r},t)$ as function of \vec{r} and t (set B, $I = 3$, $T = 300$ K)

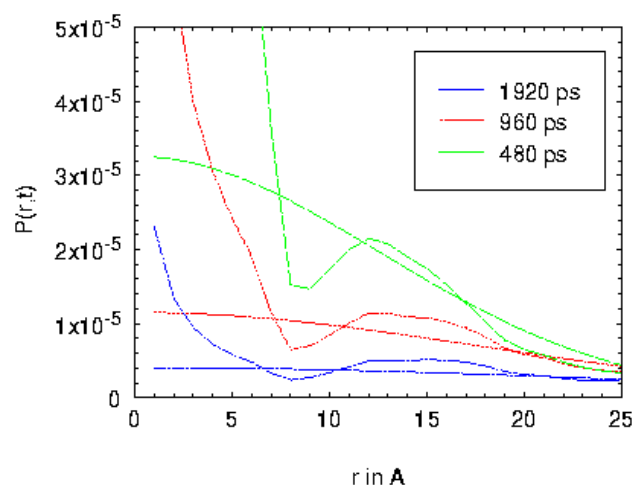


Figure 5. Propagator $P(\vec{r},t)$ for fixed times as function of \vec{r} compared with the ideal Gaussian-Propagators (set B, $I = 3$, $T = 300$ K)

while in figure 5 for three special times a comparison with the ideal Gaussian behaviour is given.

The density distribution in the cation free LTA zeolite (sometimes we use for shortness the abbreviation 'ZK4' although this is somewhat inaccurate) shown in figure 6 may well be understood by the isopotential lines [8] for this zeolite. The density distributions — here demonstrated in a plane through the center of the large cavity — show a remarkable structure. Corresponding to the potential surface these distributions are different from zero practically only near the cavity wall and these densities have maxima in the window (set A) and *in front of* them (set B), respectively.

Influence of the potential parameters on D

The influence of potential parameters on the diffusion coefficients is remarkable. Even small parameter changes may cause significant changes in the diffusion processes (Figure 8).

It has been shown that the choice of the σ parameter of the Lennard-Jones potential eq. 1 for the methane - oxygen interaction has a dramatic influence not only on the value of the diffusion coefficient but also on its concentration dependence [8].

As in [8] we use the two different potentials (A, B) from the literature based on the sets of potential parameters shown in table 1.

An impression of the shape of the potential surface, especially with respect to the different behaviour in the vicinity of the window is given in figure 7 for parameter set A (left) and set B (right), respectively. Easily can be seen that the potential values are high in the center of the large cavity and, of course, at the repulsive walls. The potential has a minimum in the window in model A and in front of the window in model B where it has a saddle point in the center of the window. This threshold reduces the diffusivity in model B. From the larger value of σ in set B for the dominating oxy-

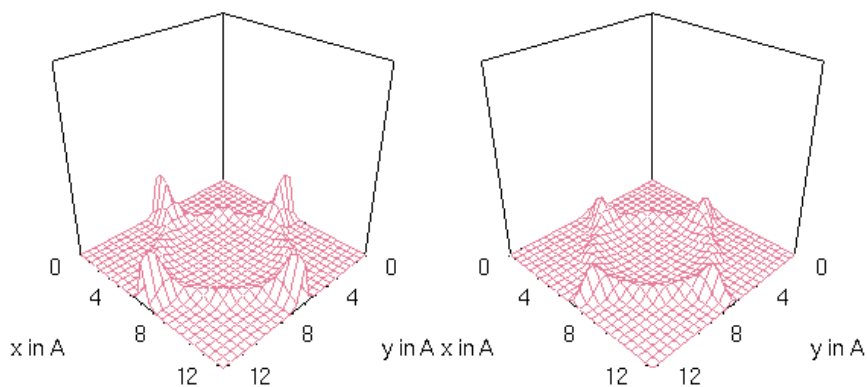


Figure 6. Density distribution of methane in a cation free LTA (left set A, right set B)

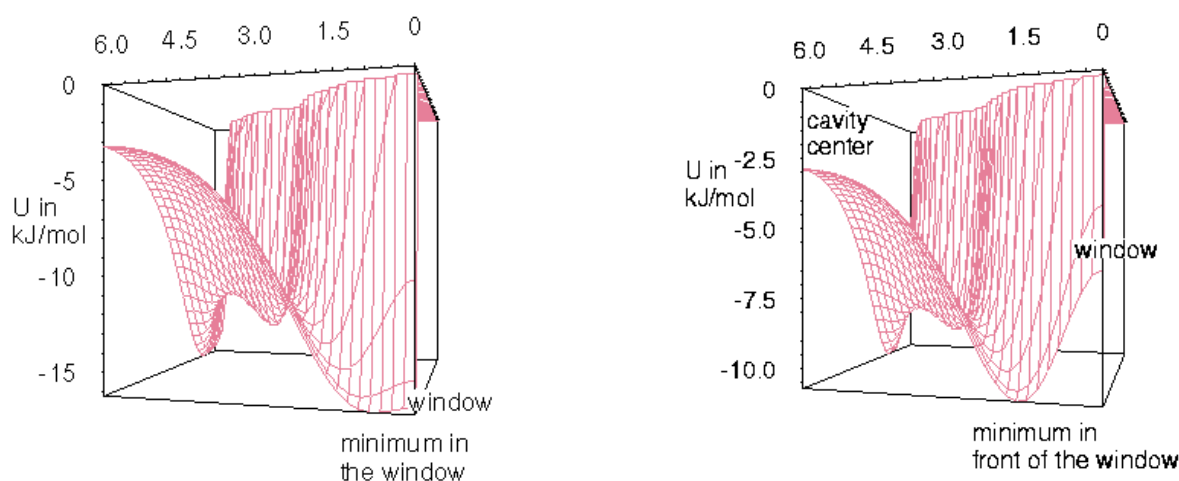
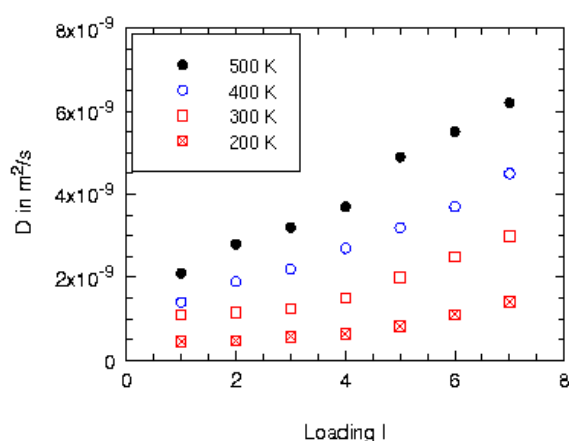


Figure 7. Potential of cation free LTA (left: set A, right set B)

gen - guest interaction in the zeolite a narrower window between adjacent cavities results. Especially for methane which has a similar size as the window this causes dramatical changes [8, 16].

This effect seems to be the consequence of the interrelation of two effects (reflexion at the inlet of the window, coming back after passing the window) with different density dependence [8, 16]. Fig. 8 (left) shows that the diffusion coefficient D increases with increasing mean number of guest molecules per cavity and temperature for set B while this dependence for set A demonstrated for $T = 173$ K is reversed (right). For higher loading this figure shows an interesting cross over of both curvatures which is under examination in detail.



Influence of cations on D

The dynamics even of small neutral molecules with saturated bindings is strongly influenced by the presence of exchangeable cations [9, 11]. For these investigations we have chosen the NaCaA zeolite with 4 Na and 4 Ca so that the windows — marked by w in fig. 2 — are free from cations. The unexpected (see [14]) strong effect can clearly be seen in fig. 9 and has been confirmed experimentally, meanwhile [17]. In comparison with the cation free LTA the self-diffusivity decreases up to two orders of magnitude.

It should be noted that the computational effort is much larger in this case than in our previous simulations for the cation free analogue zeolite since much longer trajectories (up to 5-10 ns) are necessary to evaluate such small D 's. Additionally, the calculation of the forces resulting from the polarization energy is very time expensive although we were able to replace the full Ewald sum for our system by a corrected r space part of this sum.

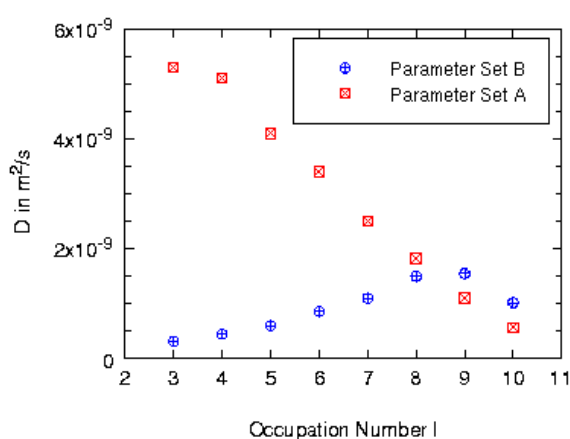


Figure 8. The diffusion coefficient for different loadings of methane in the cation free LTA zeolite (left: different temperatures, set B; right: $T = 173$ K, set A and B)

Table 1. Potential parameters

	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

Fig. 9 demonstrates MD results for different situations and compares these data with experiments. The agreement with experimental results from NMR measurements [18] is satisfactory in the case of set A (see fig. 9).

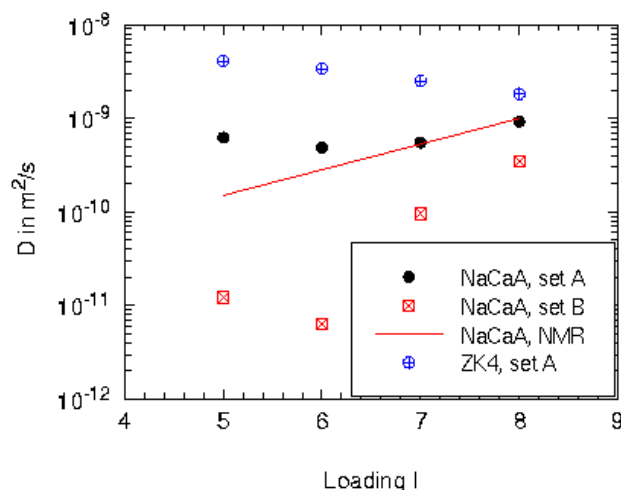
Influence of lattice vibrations on the diffusion coefficients

The influence of lattice vibrations on the diffusion coefficient in the cation free LTA zeolite is not very large for both of the parameter sets under consideration as can be seen in fig. 10. It should be noticed that the effect is small in the case of set B (smaller window) and larger in the case of set A. This is somewhat surprising. Suffritti and Demontis found a much stronger effect using a parameter set beyond the region of A and B [12].

Their parameters lead to a practically closed window and it appears reasonable to assume that temporary opening of windows by vibrations drastically increases D in such cases. All these effects are currently under examination.

Transport-diffusivity, corrected diffusivity and self-diffusivity

While the self-diffusion coefficient D_0 according to the Kubo theory may be obtained from

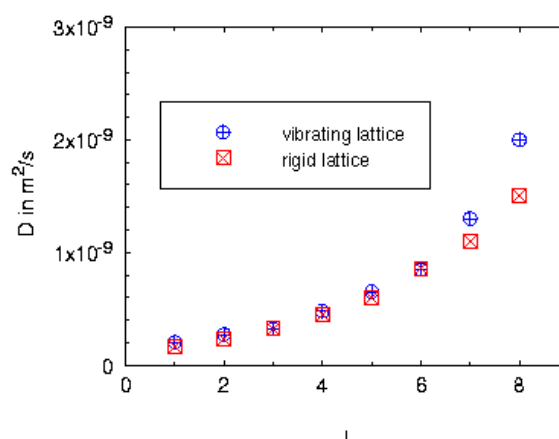
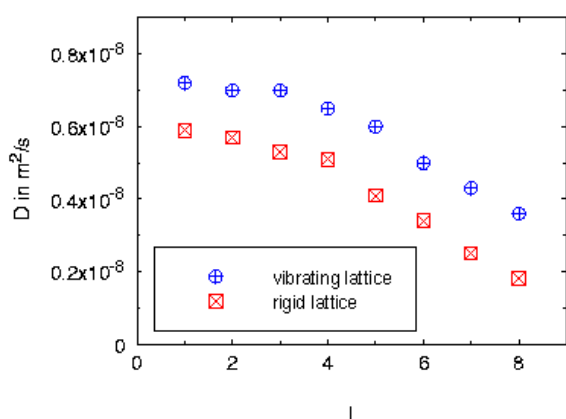
**Figure 9.** Comparison D of methane in NaCaA and cation free LTA with NMR-experiments

$$D_0 = \frac{1}{N} \sum_j \int_0^\infty dt \langle v_{zj}(0) v_{zj}(t) \rangle_0 \quad (3)$$

the so called corrected diffusion coefficient D_c includes the cross correlations between velocities of different particles.

$$D_c = \frac{1}{N} \sum_j \sum_k \int_0^\infty dt \langle v_{zj}(0) v_{zk}(t) \rangle_0 \quad (4)$$

The diffusion coefficient that appears in Fick's law usually is called transport diffusion coefficient D_T although also the other D 's are describing transport properties.

**Figure 10.** Comparison of D with rigid and vibrating lattice. (left: Set A, right: Set B)

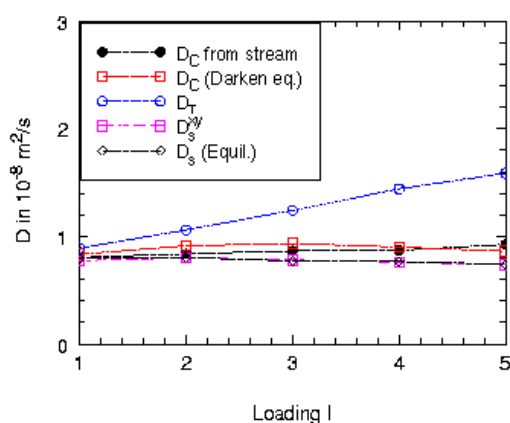


Figure 11. Self-diffusion coefficient D_s , corrected diffusion coefficient D_c and transport-diffusion coefficient D_T from nonequilibrium-MD

$$J = -D_T \frac{dn}{dx} \quad (5)$$

J is the stream and n is the density. If the gradient of the chemical potential μ is interpreted as driving force for a diffusive stream then

$$J = -nB \frac{d\mu}{dx} \quad (6)$$

where B is the mobility. According to Kubo's theory B is connected with the corrected diffusivity by the Einstein relation

$$D_c = Bk_B T \quad (7)$$

k_B is the Boltzmann constant. Comparison of eqs. 5 and 6 together with eq. 7 leads to

$$D_T = D_c \frac{n}{k_B T} \frac{d\mu}{dn} \quad (8)$$

which is a somewhat unusual form of the well known Darken equation. In fig. 11 these different D 's obtained from equilibrium and nonequilibrium MD simulations are compared with each other. The self-diffusion coefficients are obtained from the mean square displacement. D_T results from nonequilibrium simulations in which a density gradient in six layers of cavities is created by randomly inserting particles that leave the last layer into the first layer and evaluating the stream in the intermediate region. D_0^{xy} is obtained from the mean square displacement perpendicular to the density gradient. It turns out that the stream practically has no

influence on the self-diffusion in the direction perpendicular to the stream. D_c is somewhat larger than D_0 because of the collective effects expressed by the cross correlation terms in eq. 4. D_c is obtained from D_T by the Darken equation and compared with results from another nonequilibrium MD experiment. In this experiment a stream is produced by an external field. Measuring this stream D_c may be obtained from the Einstein relation eq. 7.

Acknowledgement We thank Professors Kärger, Pfeifer (University Leipzig), Wolfsberg (UCI Irvine) Suffritti, Demontis (University of Sassari), Brickmann (TH Darmstadt) and Theodorou (UCB) for stimulating discussions.

We are indebted to the Deutsche Forschungsgemeinschaft (SFB 294) for financial help. R.H. thanks the Fonds der Chemischen Industrie, Frankfurt, for financial support.

Finally, we are thankful for a grant of computer time by the Höchstleistungsrechenzentrum Jülich and the office of Academic Computing, University of California, Irvine.

References

1. Kärger, J.; Ruthven, D.M. *Diffusion in zeolites and other microporous solids*, Wiley, New York, **1992**.
2. Allen, M.P.; Tildesley, T.S. *Computer simulation of liquids*, Clarendon Press, Oxford, **1989**.
3. Haberlandt, R.; Fritzsche, S.; Peinel, G.; Heinzinger, K. *Molekulardynamik*, Vieweg, Wiesbaden, **1995**.
4. Yashonath, S.; Demontis, P.; Klein, M.L. *Chem. Phys. Lett.* **1988**, *153*, 551.
5. Fritzsche, S.; Haberlandt, R.; Kärger, J.; Pfeifer, H.; Wolfsberg, M. *Chem. Phys. Lett.* **1990**, *171*, 109.
6. Catlow, C.R.A.; Freeman, C.M.; Vessal, B.; Tomlinson, S.M.; Leslie, M. *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 1947.
7. Fritzsche, S.; Haberlandt, R.; Kärger, J.; Pfeifer, H.; Heinzinger, K. *Chem. Phys. Letters* **1992**, *198*, 283.
8. Fritzsche, S.; Haberlandt, R.; Kärger, J.; Pfeifer, H.; Heinzinger, K. *Chem. Phys.* **1993**, *174*, 229.
9. Fritzsche, S.; Haberlandt, R.; Kärger, J.; Pfeifer, H.; Waldherr-Teschner, M. *Studies in Surface Science and Catalysis*, Vol. 84, p. 2139, Elsevier Science B.V. **1994**.
10. Fritzsche, S. *Phase Transitions* **1994**, *52*, 169.
11. Fritzsche, S.; Haberlandt, R.; Kärger, J.; Pfeifer, H.; Heinzinger, K.; Wolfsberg, M. *Chem. Phys. Lett.* **1995**, *242*, 361.
12. Demontis, P.; Suffritti, G.B. *Chem. Phys. Lett.* **1994**, *223*, 355.
13. Fritzsche, S.; Haberlandt, R.; Kärger, J. *Z. phys. Chem.* **1995**, *189*, 211.
14. General Discussion during the Faraday Symposium 26 on "Molecular Transport in Confined Regions and Membranes" *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 1797.

15. Demontis, P.; Fois, E.S.; Suffritti, G.B.; Quartieri, S. *J. Phys. Chem.* **1990**, 94, 4329.
16. Fritzsche, S.; Haberlandt, R.; Hofmann, G.; Kärger, J.; Heinzinger, K.; Wolfsberg, M. *Chem. Phys. Lett.* **1996**, submitted.
17. Heink, W.; Kärger, J.; Ernst, S.; Weitkamp, J. *Zeolites* **1994**, 14, 320.
18. Heink, W.; Kärger, J.; Pfeifer, H.; Salverda, P.; Daterna, K.P.; Nowak, A. *J. Chem. Soc. Faraday Trans.* **1992**, 88, 515.