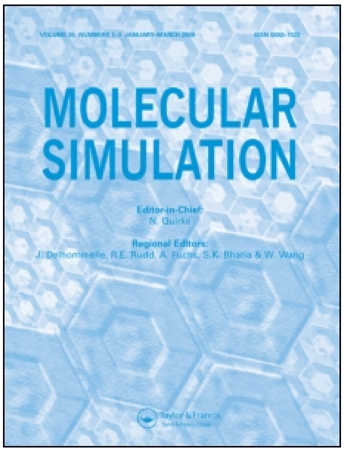
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Modelling Diffusion in Zeolites by Molecular Dynamics Simulations

S. Fritzsche; R. Haberlandt[a]; S. Jost[a]; A. Schüring[a]
[a] University of Leipzig, Faculty of Physics and Earth Sciences, Institute of Theoretical Physics, Department of Molecular Dynamics/Computer Simulations (MDC), Permoserstr, Leipzig, Germany

To cite this Article Fritzsche, S. , Haberlandt, R. , Jost, S. and Schüring, A.(2000) 'Modelling Diffusion in Zeolites by Molecular Dynamics Simulations', Molecular Simulation, 25: 1, 27 — 40
To link to this Article: DOI: 10.1080/08927020008044110
URL: http://dx.doi.org/10.1080/08927020008044110

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, 2000, Vol. 25, pp. 27–40
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

MODELLING DIFFUSION IN ZEOLITES BY MOLECULAR DYNAMICS SIMULATIONS

S. FRITZSCHE*, R. HABERLANDT, S. JOST and A. SCHÜRING

*University of Leipzig, Faculty of Physics and Earth Sciences,
Institute of Theoretical Physics, Department of Molecular Dynamics/Computer
Simulations (MDC), Permoserstr. 15, D-04318 Leipzig, Germany*

(Received April 1999; accepted May 1999)

The diffusion of molecules sorbed in zeolites is of growing interest for understanding the mechanisms of chemical processes with regard to selectivity and reactivity [1].

MD simulations give insight into physical systems on the molecular level allowing to study and visualize the motion of molecules even beyond the possibilities of experiments [2, 3]. Single system parameters can easily be varied to study their influence, also those parameters that are fixed in reality (*e.g.*, the size of particles). We present a cross section of our recent work to illustrate the capabilities of MD: The self diffusion coefficients (D) of a mixture of methane and xenon in silicalite show remarkable deviations from those of the pure species. This is shown and confirmed by PFG NMR experiments [4].

Simulating ethane in zeolite A the mechanism of diffusion has been studied. The effects of rotation on the diffusion lead to cases where D decreases with growing temperature [5].

The independence of self diffusion on lattice vibrations is proven even for zeolites with windows of guest particle size comparing simulations with rigid and vibrating zeolite lattice [6].

Keywords: Diffusion; zeolites; molecular dynamics

THE SELF DIFFUSION IN A MIXTURE

A binary mixture of methane and xenon in silicalite has been studied by MD-simulations and pulsed field gradient (PFG) nuclear magnetic resonance (NMR). Silicalite is the cation free variant of the zeolite ZSM-5. In order to study the special properties of diffusion in a mixture, the total

---

*Corresponding author. e-mail: Siegfried.Fritzsche@physik.uni-leipzig.de number of guest molecules was held constant, while the composition of the mixture was varied.

The Modell and the Experimental Technique

All interactions were modelled by 12–6 Lennard–Jones (LJ) pair potentials. The LJ parameters were taken from literature (xenon [7], methane [8]) and calculated using the rule of Lorentz–Berthelot (xenon-methane).

The silicalite lattice is assumed to be fixed. The simulations were done using the velocity Verlet algorithm with a time step of 10 fs. The simulated time was 5 ns, the MD box contained 128 guest particles with periodic boundary conditions.

The experiments were performed using the home-build PFG NMR spectrometer FEGRIS 400 [9]. PFG NMR [1] directly monitors molecular displacements and is an ideal tool to measure diffusion coefficients in adsorbate-adsorbent systems.

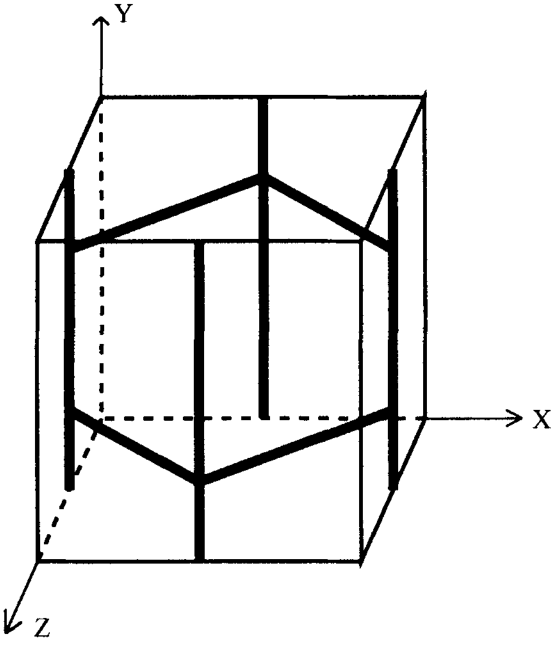


FIGURE 1 Schematic view of the channel structure of silicalite.

Results

The diffusion coefficient of pure methane in silicalite is about one order of magnitude bigger for $T = 150\,\mathrm{K}$ than the one of xenon. In the mixture xenon diffusion is nearly unaffected by the composition of the mixture, but it is affected by the total loading, while the methane diffusion gets slower with increasing xenon content. For a loading of about 8 xenon atoms per unit cell, methane diffusion is slowed down nearly to the same diffusion coefficient as xenon. The experiments show very similar results, but the diffusion coefficient of methane stays bigger than the one of xenon.

At room temperature, the diffusion coefficient of pure methane in silicalite is about five times bigger than the one of pure xenon. The mixture shows qualitatively the same behaviour as in the upper case. Due to the smaller signal intensity for xenon NMR compared with hydrogen NMR, xenon diffusion was not measurable. The results of the experiments agree well with the results of the simulations again.

The mutual influence of the two components is highly asymmetric, so we can say: diffusion in this binary mixture is dominated by xenon.

The reason for this dominance could be found in the topology of silicalite. The channel diameters are too small to allow overtaking. Therefore at high

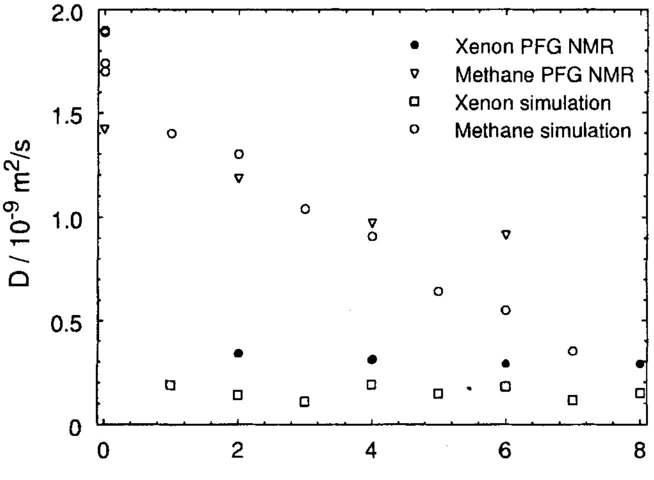


FIGURE 2 The mean diffusion coefficients of methane and xenon in different compositions of the mixture at $T = 150\,\mathrm{K}$ for a total loading of 8 particles per unit cell from simulations and experiments.

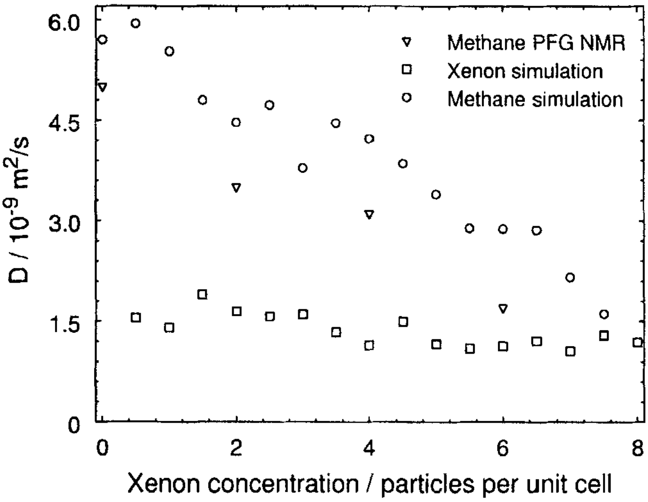


FIGURE 3 The mean diffusion coefficients of methane and xenon in different compositions of the mixture at $T = 293\,K$ for a total loading of 8 particles per unit cell from simulations and for methane from experiments, too.

xenon loadings, the faster methane molecules can move only within a cage of nearest xenon neighbours.

This leads to the question: what is the reason for the slower diffusion of xenon compared to methane?

There are two possible answers in the modell used for the simulations. The first is, xenon atoms are much heavier and therefore, at the same temperature, slower than methane molecules. The second is, the LJ interaction with the zeolite lattice is stronger for xenon, so the potential barriers are higher for xenon than for methane. To find out, which of the two reasons is dominating, we varied the computational parameters.

Variation of Computational Parameters

In comparison to the xenon diffusion, pseudoxenon1 has higher diffusion coefficients, but still much lower values than methane. Again the diffusion coefficients of the two components get closer the higher the content of pseudoxenon1 is. And once again, the composition of the mixture does not influence the diffusion of pseudoxenon in a significant way.

The habit of Figure 5 is very similar to Figure 4. The values of the diffusion coefficient of pseudoxenon2 are about 40% lower than the ones of pseudoxenon1, but the results are qualitatively equal.

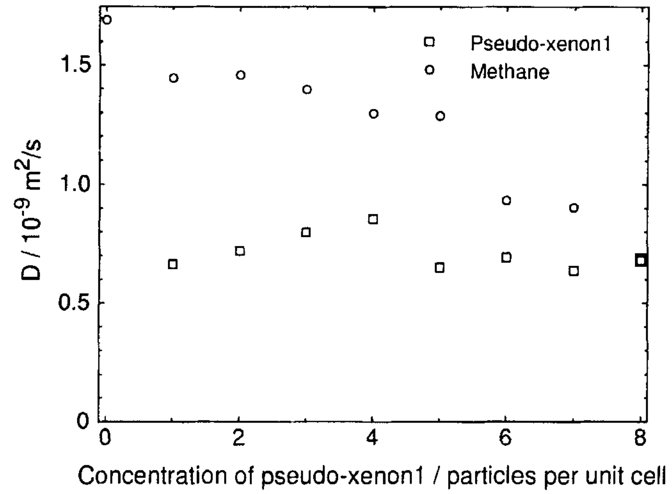


FIGURE 4 Mean diffusion coefficient in a mixture of methane and an artificial species with the mass of xenon and the LJ parameters of methane, called pseudoxenon1, at $T = 150\,\mathrm{K}$ for a total concentration of 8 particles per unit cell.

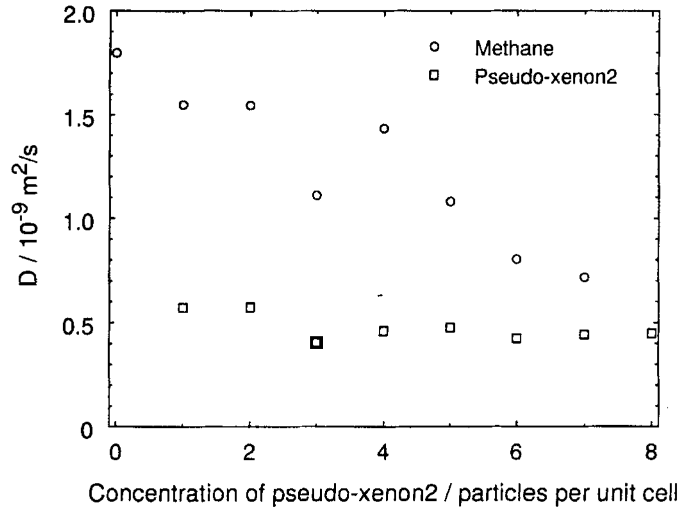


FIGURE 5 Mean diffusion coefficient in a mixture of methane and an artificial species with the mass of methane and the LJ parameters of xenon, called pseudoxenon2, at $T = 150\,\mathrm{K}$ for a total concentration of 8 particles per unit cell.

Both differences in the modell parameters between xenon and methane lead to similar effects with respect to diffusion in this mixture and the influence of both is significant.

ROTATION AND DIFFUSION

MD simulations with ethane adsorbed in an LTA zeolite structure have been carried out to study the diffusion of rotating molecules in small pore zeolites. The free diameter of the 8-ring connecting adjacent cavities is of about the size of the methyl group.

- **definition (see Fig. 6):**
  - E is the sum of the potential energies of the two centers of force
  - x is the position of the center of mass of the molecule along the window axis
  - alpha is the angle between the molecular axis and the window axis.
- **characteristics:**
  - deep minima at the zeolite walls ($3.5\,\text{Å} < x < 4.5\,\text{Å}$; $8.5\,\text{Å} < x < 9.5\,\text{Å}$)
  - a local maximum in the cavity center ($x = 0\,\text{Å}$; $x = 12.3\,\text{Å}$ respectively)
  - strong dependence on the angle alpha in the window ($4.5\,\text{Å} < x < 8.5\,\text{Å}$).
- **two sets of potential parameters:**
  - set A: [10] minimum of E for small angles alpha in the window
  - set B: [11] maximum of E for any alpha in the window
  - **aim:** study the influence of the window diameter on the self diffusion coefficient D
- **question:** how does molecular rotation influence D.

Self Diffusion Coefficients (see Fig. 7):

- D is growing with loading for $T = 500\,\text{K}$
- D is falling with loading for $T = 200\,\text{K}$
- at low loadings D is decreasing with increasing T
- at $I = 3$ there is a crossover in loading and temperature dependences of D (see Fig. 8)
- lowering the window diameter D is decreased by up to two orders of magnitude
- there is a strong temperature dependence of D for set B.

How can these Results be Explained?

The average potential energy along the window axis calculated during the MD-simulations can help (see Fig. 9):

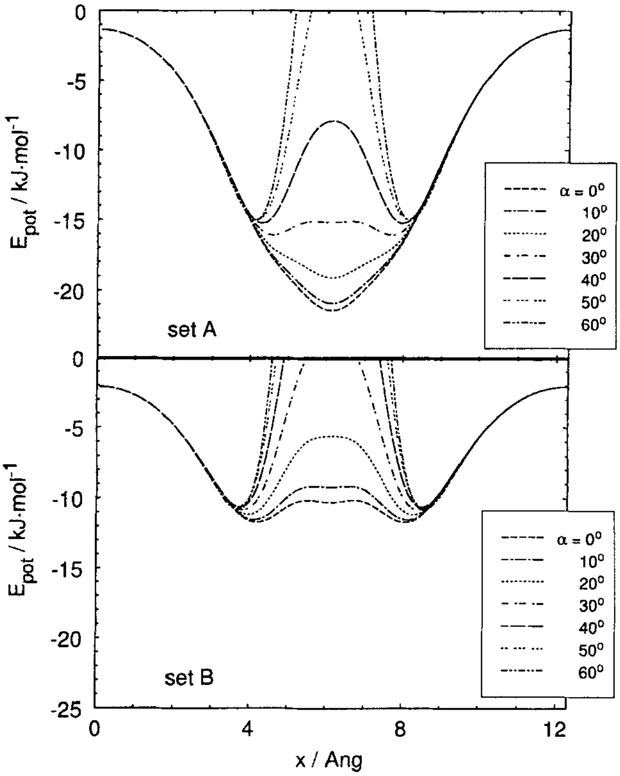


FIGURE 6 Potential of ethane in zeolite A.

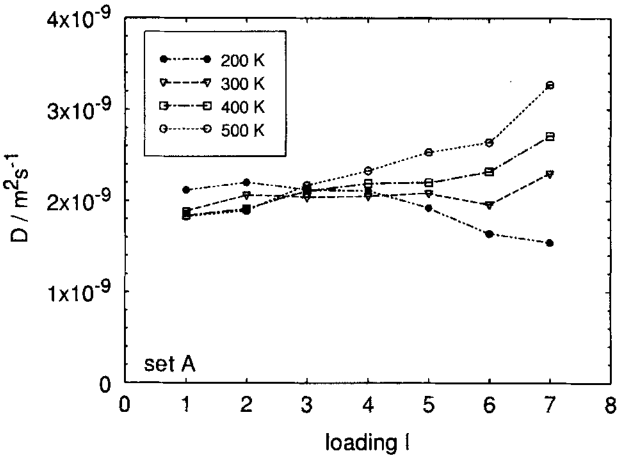


FIGURE 7 Loading dependence of the self diffusion coefficient D for different temperatures (parameter set A).

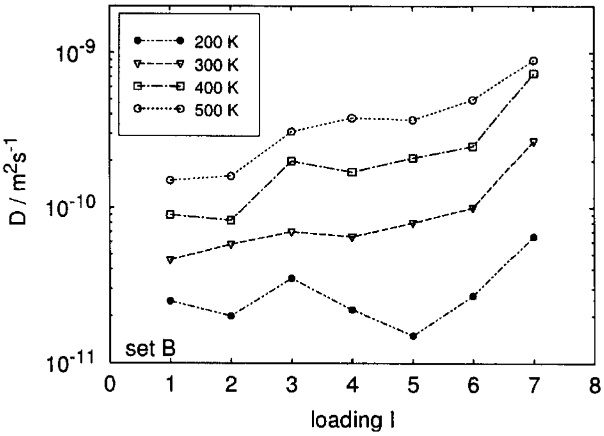


FIGURE 8 Loading dependence of the self diffusion coefficient D for different temperatures (parameter set B).

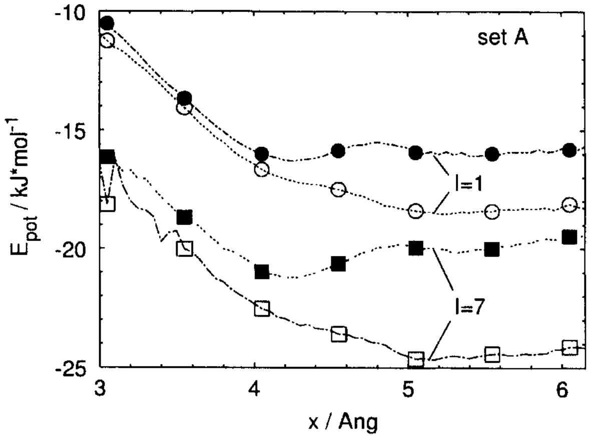


FIGURE 9 Average potential energy along the window axis for parameter set A.

- unfilled symbols: $T = 200\,K$
- filled symbols: $T = 500\,K$
- the average potential shows a potential barrier in the window entrance ($x \sim 4.5\,Å$) at $T = 500\,K$ that does not exist at $T = 200\,K$
- this effect is found at low as well as at high loadings (see Fig. 10)
- there is a high potential barrier for passing the window
- this barrier is increasing with temperature.

Why does a potential barrier occur only at high temperatures (set A)? (see Fig. 11):

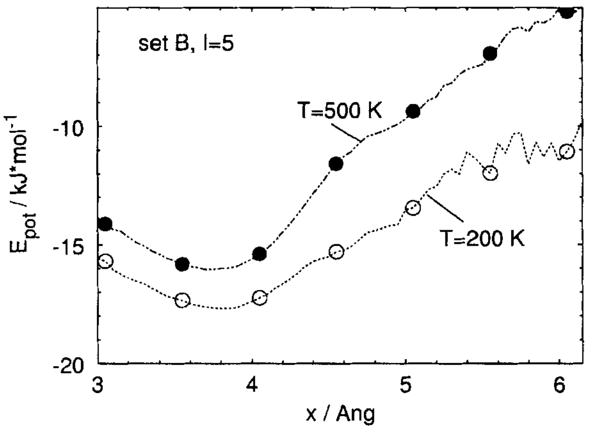


FIGURE 10 Average potential energy along the window axis for parameter set B.

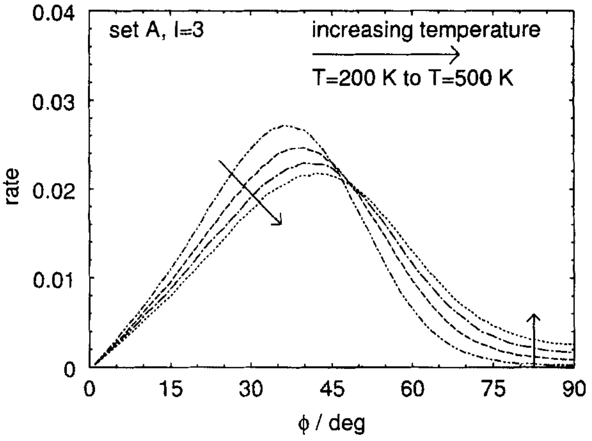


FIGURE 11 Distribution of the angle alpha occuring in the region 4.5 Å < x < 5.0 Å (compare Fig. 6).

- this region marks the window entrance
- with rising temperature more molecules with angles alpha between 60° and 90° are found
- these molecules can hardly get deeper into the window
- they contribute high potential values to the average potential.

Conclusions

- the potential barrier in the case of set B explains the Arrhenius type temperature dependence of D

- the temperature dependence of the potential barrier is responsible for the decrease of *D* with increasing *T* observed for set A at low loadings
- the temperature dependence of the angle distribution causes the temperature dependence of the potential barrier.

THE INFLUENCE OF LATTICE VIBRATIONS ON DIFFUSION

The knowledge about the influence of lattice vibrations on the migration of guest molecules in zeolites gives not only important insight into the diffusion mechanism but is also of great practical interest for MD simulations since computer time can be saved by simulations in the rigid lattice. In [12] the diffusion coefficient was found to be 12 times larger in simulations with vibrating lattice than in corresponding simulations with rigid lattice.

In earlier investigations with rigid lattice *D* for methane in the cation free A zeolite turned out to be extremely sensitive against small differences in the parameters chosen for the window size [13]. This seemed to confirm the results of [12].

But, revisiting these results they could be corrected. There is no remarkable influence of the lattice vibrations on *D* even if the windows are so small that the potential threshold hinderes the diffusion of guest molecules.

The Model

The harmonic forces between the lattice atoms are taken from the model proposed in [14, 15] (see Fig. 13).

Left: geometrical shape. Right: Arrangement of atoms and cations in the NaCaA zeolite with silicon/aluminium ratio 1:1. w means window. In the cation free form the Al atoms are replaced by additional Si atoms and the sodium and calcium ions are missing (see Fig. 12).

The elasticity of the angles is realized by additional fictive forces between oxygens that are separated by only one *T* atom.

The Central Result of [6]

Abbreviations: rig/vib – rigid/vibrating lattice,
sigma – Lennard – Jones parameter of the methane-oxygen interaction. Larger sigma means smaller window.

For all window sizes examined the *D* values for rigid and vibrating lattice agree within the range of fluctuations (see Fig. 14).

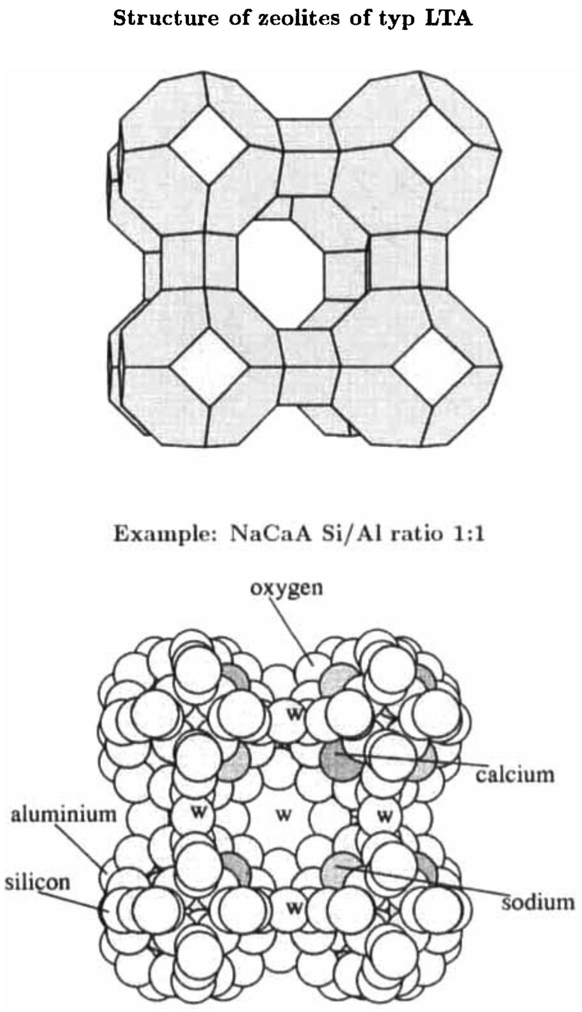


FIGURE 12 Structure of the A-type zeolites.

How can the difference in D for rigid and for flexible window that was found in [12] be explained?

This Figure 16 shows the probability distribution for the instantaneous values of the two window diameters defined in Figure 15 for two special cases. One case is the lattice with Si, Al and the other one the pure silicon version.

While in [12] lattice coordinates from the literature have been used for the rigid lattice in [6] the rigid lattice was created by energy minimisation

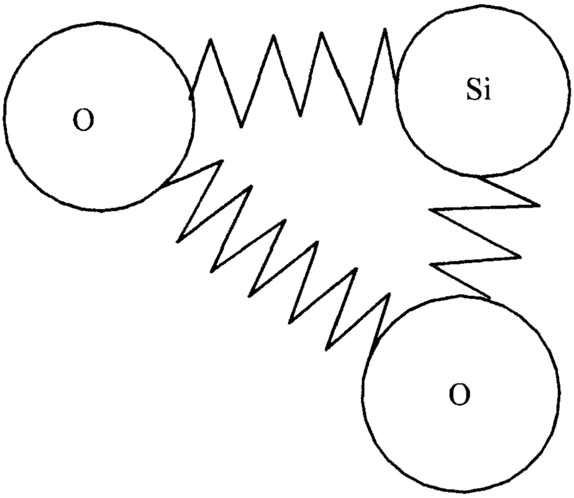


FIGURE 13 The elasticity of the lattice is realized by a harmonic central force model.

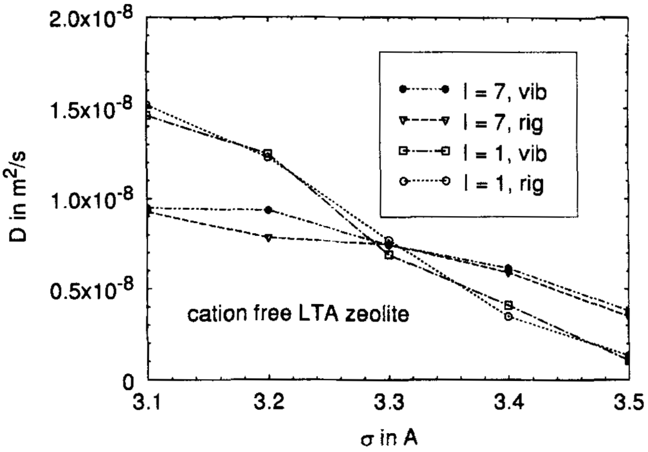


FIGURE 14 The self diffusion coefficient for the rigid (rig) and the vibrating (vib) lattice in dependence on the window size. σ is the Lennard–Jones size parameter for the CH_4—O interaction.

(cooling down). Therefore in [6] the rigid and the vibrating lattice are truly equivalent (see Fig. 17).

The dashed lines indicate the values of the two diameters which result if the lattice coordinates of the NaA are taken from the literature. While the difference in *d*1 can be neglected the difference in *d*2 causes the different values of *D* found in [12] for the rigid and the vibrating lattice, respectively.

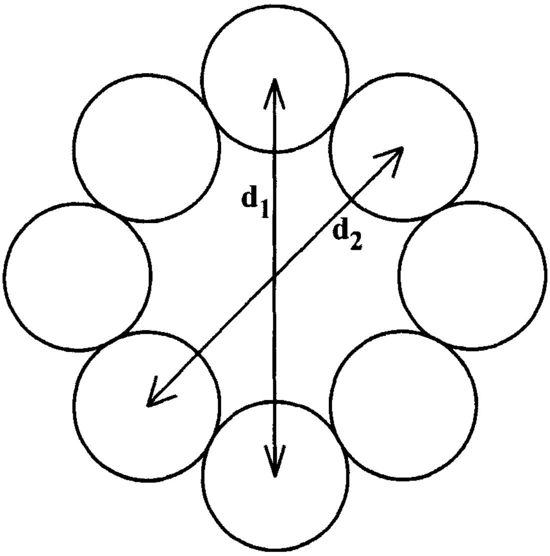


FIGURE 15 The window that connects two adjacent cavities in the zeolite can be characterized by two slightly different diameters.

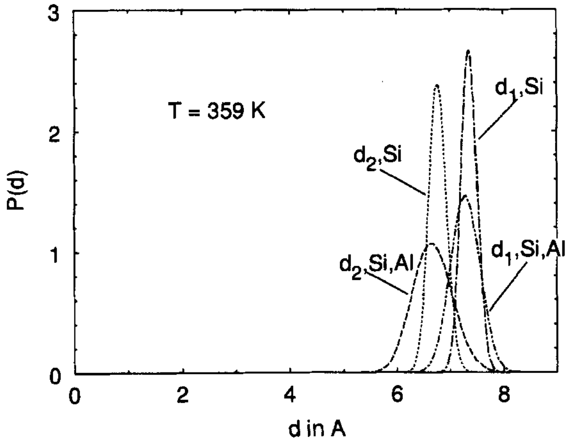


FIGURE 16 The histogram of the window diameters at 359 K.

D is extremely sentitive with respect to the window diameter in this system since the particle size and the window diameter are nearly the same.

Since the Si—O bond length is somewhat smaller than the Al—O bond the window is slightly larger in the pure silicon A-zeolite for which no lattice coordinates exist in the literature.

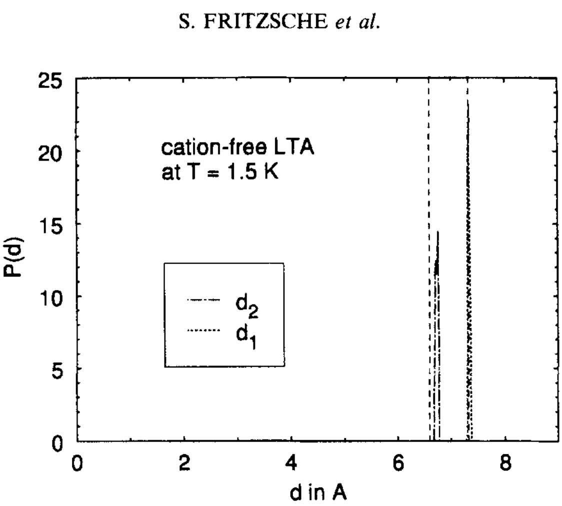


FIGURE 17 The histogram of the window diameters for the pure silicon case at 1.5 K.

References

[1] Ruthven, D. M. and Kärger, J. (1992). *Diffusion in zeolites and other microporous materials*, Wiley, New York.

[2] Allen, M. P. and Tildesley, D. J. (1989). *Computer simulation of liquids*, Clarendon Press, Oxford.

[3] Haberlandt, R., Fritzsche, S., Peinel, G. and Heinzinger, K. (1995). Molekulardynamik– Grundlagen und Anwendungen mit einem Kapitel über Monte-Carlo-Simulationen von H. L. Vörtler, Vieweg, Wiesbaden.

[4] Jost, S., Bär, N. K., Fritzsche, S., Haberlandt, R. and Kärger, J. (1998). *J. Phys. Chem. B*, **102**, 6375.

[5] Schüring, A., Fritzsche, S. and Haberlandt, R., in preparation.

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

[7] Pickett, S. D., Nowak, A. K., Thomas, J. M., Peterson, B. K., Swift, J. F. P., Cheetham, A. K., den Ouden, C. J. J., Smit, B. and Post, M. F. M. (1990). *J. Phys. Chem.*, **94**, 1233.

[8] Goodbody, S. J., Watanabe, K., MacGowan, D., Walton, J. P. R. B. and Quirke, N. (1991). *J. Chem. Soc., Faraday Trans.*, **87**, 1951.

[9] Kärger, J., Bär, N.-K., Heink, W., Pfeifer, H. and Seiffert, G. Z. (1995). *Naturforsch. A*, **50**, 186.

[10] Bezus, A. I. *et al.* (1978). *J. Am. Chem. Soc., Faraday Trans. II*, **74**, 367.

[11] Ruthven, D. M. and Derrah, R. I. (1972). *J. Chem. Soc., Faraday Trans. I*, **68**, 2332.

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

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

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

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