

An MD simulation on the applicability of the diffusion equation for molecules adsorbed in a zeolite

S. Fritzsche^a, R. Haberlandt^a, J. Kärger^b, H. Pfeifer^b and K. Heinzinger^c

^a *Research Group Statistical Theory of Non-Equilibrium Processes, WIP, KAI e.V., Permoserstrasse 15, O-7050 Leipzig, Germany*

^b *Department of Physics, Leipzig University, Linnéstrasse 5, O-7010, Germany*

^c *Max Planck Institute of Chemistry, Saarstrasse, W-6500 Mainz, Germany*

Received 19 June 1992

Diffusion of methane in a cation-free analog of zeolite A is studied by molecular dynamics (MD). The first four moments of the particle displacement profiles are evaluated by MD and compared with expressions derived from the solution of the diffusion equation. Diffusion coefficients from these expressions are found to coincide with each other for times larger than 30–60 ps depending on the occupation number.

1. Introduction

In view of the consistency of information provided by pulsed field gradient (PFG) NMR on intracrystalline self-diffusion in zeolites [1] and the agreement with the results of other experimental techniques such as inelastic neutron scattering [2] and ²H NMR [3], today there is no doubt on the validity of the picture of molecular redistribution in zeolitic adsorbant–adsorbate systems as provided by PFG NMR [4,5]. However, for some adsorbant–adsorbate systems the thus determined self-diffusivities appear to be larger by several orders of magnitude than the transport diffusivities determined in well-documented transient sorption measurements [5,6], where the typical sources of error of the earlier transient sorption experiments (bed diffusion, finite rate of sorption heat release [1,7,8]) can be assumed to be definitely excluded. A clarification of these inconsistencies is complicated by the small overlap of the ranges of measurement of the two methods [7,9].

An alternative method to study molecular migration in adsorbant–adsorbate systems is provided by

molecular dynamics (MD) [10,11], which may be very helpful, therefore, to establish quite general laws of mass transfer in adsorbant–adsorbate systems (including a structure related interpretation of the patterns of the concentration dependence of the intracrystalline diffusivities [1,4,5]), and to elucidate the origin of the differences between the transient sorption measurements and PFG NMR.

Starting with the paper by Yashonath et al. [12], in the last few years a series of MD studies have been devoted to diffusion in zeolites [13–20]. It could be shown that thermalization of guest molecules is essentially brought about by their mutual interaction [14] so that in a first-order approximation the adsorbate molecules may be treated as if being contained in a rigid framework. This result has been confirmed by comparative MD studies with rigid and flexible frameworks [15,16], and is of great importance for keeping the calculation times within reasonable limits. A satisfactory agreement between the MD diffusivities [16–20] and the PFG NMR data [5,21] has been obtained for zeolite ZSM-5.

2. Methodology

Instead of the often used integration of the veloc-

Correspondence to: H. Pfeifer, Department of Physics, Leipzig University, Linnéstrasse 5, O-7010 Leipzig, Germany.

ity autocorrelation function, Einstein's equation

$$\langle (\mathbf{r} - \mathbf{r}_0)^2 \rangle = 6Dt \quad (1)$$

may be applied to determine the diffusivity by considering the time derivative of the mean square displacement [10]:

$$D = \frac{1}{6} \frac{d}{dt} \langle (\mathbf{r} - \mathbf{r}_0)^2 \rangle. \quad (2)$$

Solving the diffusion equation for an infinite system, the probability density of finding a particular particle at time t at position \mathbf{r} , if it has been at position $\mathbf{r} = \mathbf{r}_0$ at time $t=0$, is found to be

$$P(\mathbf{r}, \mathbf{r}_0, t) = (4\pi Dt)^{-3/2} \exp\left(-\frac{(\mathbf{r} - \mathbf{r}_0)^2}{4Dt}\right). \quad (3)$$

Eq. (1) follows directly from eq. (3) as the second "moment" of the distribution curve of molecular displacements, where the n th moment is defined by the relation

$$\langle |\mathbf{r} - \mathbf{r}_0|^n \rangle = \int |\mathbf{r} - \mathbf{r}_0|^n P(\mathbf{r}, \mathbf{r}_0, t) d\mathbf{r}. \quad (4)$$

As a sufficient condition for the validity of the diffusion equation the complete space and time dependence of eq. (3) must be fulfilled. This means in particular that the time dependence of all moments must be compatible with eq. (3). With the definition given by eq. (4) one obtains for the first, third and fourth moments of the distribution curve

$$\langle |\mathbf{r} - \mathbf{r}_0| \rangle = 4 \sqrt{Dt/\pi}, \quad (5)$$

$$\langle |\mathbf{r} - \mathbf{r}_0|^3 \rangle = \frac{32(Dt)^{3/2}}{\sqrt{\pi}}, \quad (6)$$

$$\langle (\mathbf{r} - \mathbf{r}_0)^4 \rangle = 60(Dt)^2. \quad (7)$$

In analogy to the treatment with the second moment (eqs. (1) and (2)) any of these time dependences may be used to determine the diffusivity D . Apparently, these quantities will only coincide with each other if the distribution curve is in fact given by eq. (3). A comparison of the diffusivities derived from different moments may serve, therefore, as a test of the validity of the diffusion equation on intracrystalline zeolitic diffusion.

Since the particles move preferentially along the cavity walls (see below) this motion is not isotropic for short times. Only in a long time limit when each

particle moved through different cavities can an isotropic behaviour be expected because of the cubic symmetry of the zeolite under consideration.

3. Results and discussion

In our MD simulations, we have considered methane in a cation-free analog of zeolite A (called ZK4) with a silicon to aluminium ratio equal to infinity. This is a very suitable model system for systematic MD studies since complications due to diffusion anisotropy (as in the case of ZSM-5 [17-20]) and cation interaction are excluded. For the calculation of the intracrystalline potential energies and forces the interaction parameters given in ref. [22] have been used. The resulting intracrystalline potential profile is illustrated by fig. 1 showing the isopotential lines for a single methane molecule in a plane through the centre of a large cavity and four windows. Since the potential energy in the centre of the cavity is higher by about 8 kJ/mol than in the vicinity of the walls, positions in the centre of the cavities will only be occupied at higher loadings. The sites of lowest potential energy (about -15 kJ/mol) are located near the center of the windows between adjacent cavities, while high positive values of the potential energy (up to infinity) will be found at the cavity walls.

The MD calculations have been performed on the CRAY-Y-MP at the Hochleistungsrechenzentrum of the Forschungszentrum Jülich. We used the velocity version of the Verlet algorithm [10], approximating the methane molecules and lattice atoms by spherical Lennard-Jones centres. Owing to this simplification and the rigid-lattice approximation, the MD box could be chosen to contain as much as 64 large cavities. For a loading of 1 molecule per cavity even 125 cavities could be included.

Periodical boundary conditions have been applied. The time increment was 5×10^{-15} s. In all cases equilibration runs of 20000 steps have been carried out before starting the evaluations. The length of the evaluation part of the runs was 150000 time steps. The large number of cavities and hence of guest molecules ensured a relatively high accuracy in the obtained D values (about 3%), and simultaneously allowed realistic fluctuations in the cavity occupation. The data presented in fig. 2 reveal remarkably broad

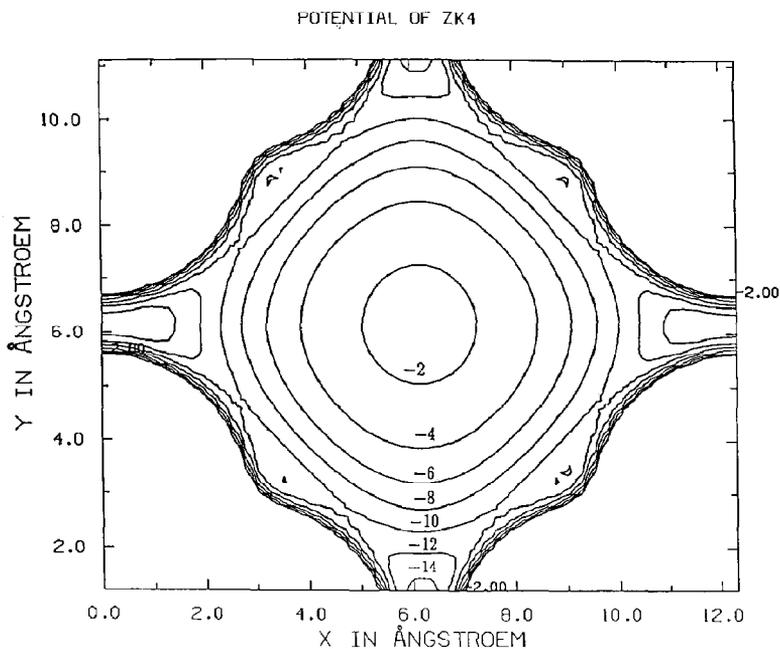


Fig. 1. Isopotential lines for a single methane molecule in a plane through the centres of a large cavity and four windows for the cation-free analog of zeolite A (potential energy is in kJ/mol).

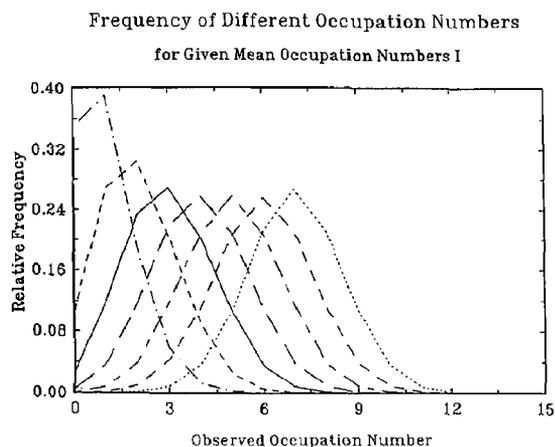


Fig. 2. Distribution of the occupation numbers of the cavities in the model zeolite for MD runs with mean occupation numbers $I=1-7$: (·-·) $I=1$; (- - -) $I=2$; (—) $I=3$; (- - -) $I=4$; (- - -) $I=5$; (- - -) $I=6$; (···) $I=7$.

distribution curves for the occupation numbers. Such fluctuations would be suppressed by the periodical boundary conditions if the MD box contained only few cavities.

To be able to compare runs for different numbers of molecules at the same temperature we introduced a weak thermalization as proposed by Berendsen et al. [23]. Only with a correct temperature adjustment can unambiguous information about the concentration dependence of self-diffusion result. In ref. [23] it has been shown for which strength of thermalization the dynamic and static properties of the system are not affected. We found that in our case even a ten times weaker thermalization than that given in ref. [23] was sufficient to guarantee an average value of the temperature to within less than 0.5 K of the desired value. We confirmed that the procedure of thermalization had no influence on the behaviour of the system by additional tests: by a moments analysis the velocity distribution was found to be in good agreement with a Gaussian curve, and a comparison of diffusion coefficients obtained from unthermalized and thermalized runs at the same temperature showed agreement within the limits of accuracy.

In this Letter, the self-diffusivities have been calculated on the basis of eqs. (1) and (5)–(7) from the first four moments of the distribution curves of

the molecular displacement in order to examine the validity of the diffusion equation.

As an example, fig. 3 shows the diffusivities calculated in this way at 300 K for mean occupation numbers 1, 3 and 7 molecules per cavity in dependence on the observation time. In these cases the diffusivities were found to approach each other after about 30–60 ps. One has to conclude, therefore, that for times larger than 30–60 ps molecular propagation is already described by distribution curves of the

form of eq. (3) indicating that a kind of hydrodynamical stage has been reached. Since we found [24] that a methane molecule stays in mean about 5–10 ps in one cavity this result seems to be reasonable. The concentration dependence of the diffusion coefficient and several other features of the diffusion mechanisms as residence times in single cavities and trajectory studies will be discussed extensively elsewhere [24].

Acknowledgement

We thank Professor Brickmann and Mr. Schimpf, TH Darmstadt, for stimulating discussions and the HLRZ Jülich for the opportunity to use the Cray-Y-MP and for support. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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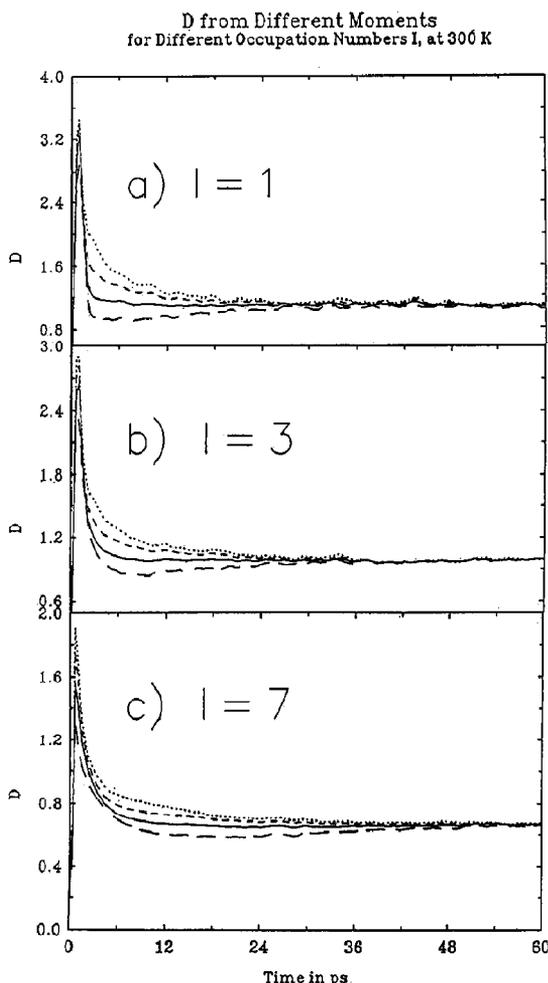


Fig. 3. Self-diffusivities of methane in the model zeolite at 300 K for mean occupation numbers of 1 (a), 3 (b) and 7 (c) molecules per cavity determined from the first four moments ($n=1-4$) of the distribution curves of molecular displacements simulated in MD calculations in dependence on the observation time. D is in $10^{-8} \text{ m}^2/\text{s}$; (---) $n=1$; (—) $n=2$; (- - -) $n=3$; (···) $n=4$.

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