Single-File Diffusion Observation

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Molecular diffusion in zeolites of unidimensional channel structure is studied by pulsed field gradient NMR. In contrast to ordinary diffusion, the mean square displacement increases in proportion with the square root of the observation time. This behavior is explained by assuming that the molecules are unable to pass each other (“single-file” diffusion). The diffusivity of an isolated molecule estimated from the mobility in the single-file system is 2 orders of magnitude larger than the largest intracrystalline diffusivities in zeolites so far observed. The finding is supported by both the observed concentration dependence and molecular dynamics simulations.

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Particle diffusion in systems of reduced dimensionality exhibits a number of peculiarities in comparison with the unconfined three-dimensional space [1–4]. Even for such an apparently simple system as a set of particles moving in one dimension in a confining box, molecular simulations lead to transport patterns which are in no way predictable on the basis of classical, macroscopic conceptions [5]. Interestingly enough, the large amount of profound theoretical work is in striking contrast with a rather limited number of experimental studies.

Molecules in zeolite molecular sieves [6] may serve as a suitable model system for an experimental study of molecular diffusion under structural confinement. Zeolites with long unconnected parallel channels should be a quite good realization of the theoretically investigated one-dimensional systems. On the other hand, zeolites are of crucial importance as key materials for important technical processes such as heterogeneous catalysis, molecular separation, and cation exchange, and offer excellent prospects for an application as host systems for the fabrication of novel photonic or optical materials [7].

Being able to determine the probability distribution of molecular displacement, pulsed field gradient (PFG) NMR spectroscopy is a sensitive method for the study of molecular diffusion in heterogeneous media [8,9]. We have applied this method for diffusion studies with tetrafluoromethane in zeolite $AlPO_4$-5. $AlPO_4$-5 is traversed by parallel channels. The channel diameter as resulting from a structure analysis by x-ray diffraction is of the order of 0.73 nm [6,10], whereas the diameter of the CF_4 molecules is 0.47 nm [11]. With these diameters, a mutual passage of the molecules should be excluded. The PFG NMR measurements have been carried out by means of the home-built spectrometer FEGRIS 400 [12] operating at a ^{19}F resonance frequency of 376 MHz, with field gradient amplitudes up to 24 T/m. The measuring temperature of 180 K was chosen as a compromise between the requirement of small gas phase concentration (which decreases with decreasing temperature) and the finite supply of liquid nitrogen within the cooling system. The zeolite sample was contained in glass tubes with an outer diameter of 8 mm at a filling height of about 12 mm. The molecular mean square displacement $\langle z^2 \rangle$ along the channels during the observation time t has been determined from the best fit of the theoretical expression for the PFG NMR signal attenuation Ψ due to diffusion in straight channels with statistical orientation [8,13]

$$\Psi = \frac{1}{2} \int_{-1}^{1} dx \exp[-\gamma^2 \delta^2 g^2 \langle z^2(t) \rangle x^2/2] \qquad (1)$$

to the experimental data, where δ, g, and t denote, respectively, the width, amplitude, and separation of the field gradient pulses. γ stands for the magnetogyric ratio. δ was varied between 0.3 and 0.8 ms. Equation (1), which has been derived originally for the case of normal diffusion, is easily shown to also follow under the more general assumption that the probability of molecular displacement is governed by a Gaussian distribution [8,13]. The signal attenuation was generally followed over 1 order of magnitude. In this range, within the uncertainty of the measurements, virtually no deviation from Eq. (1) could be observed. A slightly steeper decay as predicted by Eq. (1) was observed only in the very first part of the attenuation plot . This decay may be attributed to a small fraction of molecules exchanging between the zeolite crystallites.

Figure 1 shows the resulting mean square displacement $\langle z^2 \rangle$ for CF_4 in $AlPO_4$-5 at 180 K as a function of the observation time t for four different occupancies of the channel system. The observed time dependence is in striking contrast to the case of normal diffusion, where the mean square displacement increases in proportion with t, and which has been found in all so far investigated zeolitic adsorbate-adsorbent systems [9]. In zeolites with a unidimensional channel network, normal diffusion should only occur if the molecules are able to pass each other during the observation time. If this is not the case, molecular displacements in one direction will be followed by a displacement in the opposite direction with a higher probability than by a displacement in the same direction. The

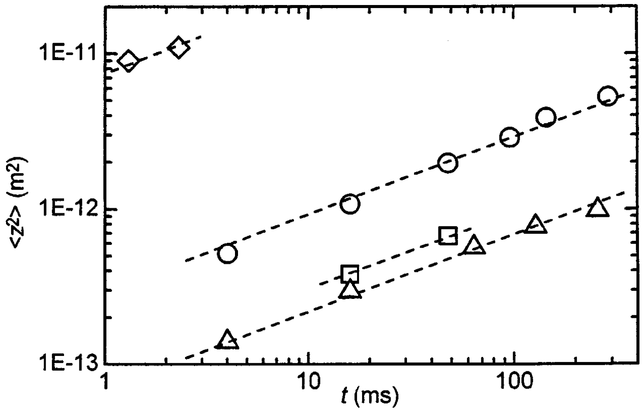

FIG. 1. Molecular mean square displacement of CF_4 in $AlPO_4$-5 at 180 K as a function of the observation time at a sorbate concentration of 0.005 (◇), 0.05 (○), 0.2 (□), and 0.4 (△) molecule per unit cell.

experimental evidence reflected by Fig. 1 may be explained, therefore, by assuming that for the investigated system during the observation time a mutual passage of the diffusants in the interior of the individual channels is excluded. Systems of this type have been termed single-file systems [14,15]. Molecular transport in single-file systems has been the subject of numerous theoretical investigations [1–3,16,17].

By assuming a simple random walk model, the molecular mean square displacement in single-file systems has been shown to be proportional to the square root of the observation time [1,3,16]. Moreover, the displacements are found to be governed by a Gaussian distribution [16,17]. This justifies the application of Eq. (1) for data analysis, which is additionally supported by the fact that experimental data are in complete agreement with the theoretical approach [18]. The time dependence of single-file diffusion is astonishingly well reflected by the experimental data shown in Fig. 1.

For displacements up to the order of 2 μm the proportionality is nearly ideally fulfilled. This fact may be interpreted as a hint that imperfections in the channel structure do not disturb the expected diffusional behavior. The existence of imperfections could lead either to the possibility that particles can change their relative order thus effecting a breakdown of the single-file condition or to a blocking of certain positions in the channel and thus to a confinement of the maximum displacements. Because there is no deviation from the expected behavior, the concentration of both types of imperfections seems to be very small. In this way, PFG NMR is able to provide direct information about the permeability of the zeolite structure. Since the concentration of the lattice imperfections leading to a reduced permeability may be far below the range accessible by x-ray diffraction, this information is unique and cannot be provided by conventional techniques of structure analysis.

Molecular transport in single-file systems may be understood as the combined effect of the motion of the individual molecules and their mutual confinement. On the basis of this consideration, the long time behavior of the molecular mean square displacement in a single-file system may be related to the displacement which a molecule would undergo if any interaction with other molecules is excluded, by the simple expression [17]

$$\langle z^2(t)\rangle = l\langle|s(t)|\rangle, \tag{2}$$

where $\langle|s(t)|\rangle$ denotes the mean value of molecular displacement if there were only one molecule in the system, and l stands for the mean free distance (clearance) between adjacent molecules. Long time behavior is understood as the behavior after the onset of single-file behavior, which is approximately attained after the time that a particle needs to move over the mean free distance. Equation (2) holds true for any type of motion for an isolated molecule, for instance, for a deterministic motion, where $\langle|s(t)|\rangle \propto t$, or for a diffusive behavior, where $\langle|s(t)|\rangle \propto \sqrt{t}$. Furthermore, no assumptions on the shape of the propagator of the free particle must be made for the derivation of Eq. (2).

In a zeolite channel, the movement of an isolated particle will—after a short ballistic period—generally be determined by the stochastic interaction with the channel walls yielding diffusional behavior. In this case the propagator is a Gaussian and the mean square displacement is given by the Einstein relation $\langle s^2(t)\rangle = 2Dt$, where

$$\langle|s(t)|\rangle = \sqrt{\frac{4D}{\pi}}\sqrt{t}\,. \tag{3}$$

Introducing the single-file mobility factor F by the relation [15]

$$\langle z^2(t)\rangle = 2F\sqrt{t} \tag{4}$$

and inserting Eqs. (3) and (4) into Eq. (2) yields

$$D = \pi\frac{F^2}{l^2}\,. \tag{5}$$

Table I presents the results of Fig. 1 in terms of the respective single-file mobility factors and the corresponding diffusivities calculated on the basis of Eq. (5). The clearance l between adjacent molecules has been calculated from the relative pore occupancy θ and the estimated value for the mean diameters σ of the adsorbate molecules (0.47 nm for CF_4 [11]) by assuming a perfect unidimensional arrangement of the molecules within the channels:

$$l = \frac{1-\theta}{\theta}\,\sigma\,. \tag{6}$$

The diffusivities estimated on the basis of Eq. (5) should result if it were possible to measure at infinitely low sorbate concentrations. It is interesting to note that the data given in Table I are about 2 orders of magnitude larger

TABLE I. Results of the PFG NMR self-diffusion studies with CF_4 adsorbed in $AlPO_4$-5 at 180 K, represented in terms of the single-file mobility factor F [cf. Eq. (4)] and the limiting diffusivity [cf. Eq. (5)]. The mean free distance l is calculated according to Eq. (6). The errors of the experimental values are about 50%.

c (mol./unit cell)	l (nm)	F ($m^2\,s^{-1/2}$)	D ($m^2\,s^{-1}$)
0.4	1.63	0.7×10^{-12}	0.6×10^{-6}
0.2	3.73	1.5×10^{-12}	0.5×10^{-6}
0.05	16.3	4.5×10^{-12}	0.3×10^{-6}
0.005	167	1.0×10^{-10}	1.1×10^{-6}

than the largest zeolitic diffusivities for CF_4 so far measured under comparable conditions [19,20]. All these diffusion measurements have clearly been carried out at finite sorbate concentrations. It turned out, however, that for sufficiently small sorbate concentrations the diffusivities tended to approach a limiting value. This may be easily attributed to the fact that in all these studies zeolites with a higher-dimensional pore network were considered, where the mutual confinement of the diffusants as observed for single-file systems does not occur.

For molecular propagation in the straight channels of $AlPO_4$-5, however, the situation is completely different. According to Eq. (2), one should expect an increase in the translational molecular mobility F in proportion with the clearance l which is equivalent with the postulate that the diffusion coefficient D for infinite dilution as resulting from Eq. (5) should be the same starting from any concentration. We have checked this prediction by PFG NMR measurements with CF_4 in $AlPO_4$-5 at 180 K over a wide range of sorbate concentrations c (cf. Table I). For the concentrations 0.4, 0.2, and 0.05 molecule per unit cell the prediction is clearly fulfilled, whereas the diffusion coefficient obtained for a concentration of 0.005 molecule per unit cell seems to be too large. This deviation should be attributed to experimental uncertainties. As a consequence of the extremely low loading, the uncertainty in these measurements is of the order of a factor of 2 with respect to both the sorbate concentration and the mobility factor. The obtained agreement between theoretical prediction and experimental findings is a further confirmation of the fact that the diffusion of CF_4 in $AlPO_4$-5 follows the rules of single-file diffusion, as well as of the high translational mobility of noninteracting molecules in the straight channels of $AlPO_4$-5.

The large molecular mobility in $AlPO_4$-5 may be rationalized as the effect of molecular guidance by the channels. PFG NMR measurements with zeolites of different structure type but with parallel channels of comparable size (theta-1, mordenite [6]) are in qualitative agreement with the present finding [21], so that the enhancement of molecular mobility in one-dimensional channels in comparison with higher-dimensional pore networks appears to be a quite general effect.

While molecular dynamics (MD) simulations of molecular diffusion in zeolites with higher-dimensional networks are a well-established topic of current research [22], literature provides only a few examples of MD simulations in single-file systems [23,24]. Since in these studies real adsorbate-adsorbent systems were considered, the applied potentials were too complicated to allow the simulation over observation times, which were long enough to trace indications of single-file diffusion. In order to confirm both the time dependence of the mean square displacement and the order of magnitude of the mobility factor to be expected for systems similar to those considered in this study, we have carried out MD simulations in a model single-file system, characterized by the following parameters.

The sorbate-sorbate interaction assuming tetrafluoromethane as an adsorbate was simulated by the usual Lennard-Jones potential [25] with a particle diameter of $\sigma_{CF_4} = 0.47$ nm. The interaction between the adsorbate molecules and the zeolite lattice was simulated by a steep-wall potential

$$V_Z(\rho, z) = \begin{cases} 4\epsilon_Z\left[\left(\frac{\rho}{\sigma_Z}\right)^{12} - \left(\frac{\rho}{\sigma_Z}\right)^{6}\right] & \text{for } \rho > \rho_c\,, \\ 0 & \text{for } \rho < \rho_c\,, \end{cases} \tag{7}$$

where ρ denotes the distance between the axis of the channel and the center of the tetrafluoromethane molecule. The cutoff is at $\rho = \rho_c \equiv \sigma_Z/\sqrt[6]{2}$, where the potential has its minimum. The parameter σ_Z is related to the channel diameter d by

$$d = 2\sigma_Z + \sigma_{CF_4}\,, \tag{8}$$

and, with $d = 0.73$ nm [6,10], becomes $\sigma_Z = 0.13$ nm. To reflect the periodic structure of the zeolite lattice, σ_Z is assumed to vary periodically:

$$\sigma_Z = \sigma_{Z,0} + \Delta\sigma_Z \cos\left(\frac{2\pi z}{\lambda}\right). \tag{9}$$

Because of the fact that there are two 12 rings in a unit cell of length $c = 0.84$ nm, the periodicity was set to $\lambda = c/2 = 0.42$ nm. The calculations were carried out with three different values for the amplitude ($\Delta\sigma_Z =$ 0.010, 0.015, and 0.025 nm). Figure 2 shows the results of the MD simulation carried out at 180 K for a relative occupancy $\theta = 0.11$ corresponding to a concentration c of 0.2 molecule per unit cell.

After the initial ballistic phase with $\langle z^2\rangle \propto t^2$ there is a broad transition region to the final dependence $\langle z^2\rangle \propto \sqrt{t}$. The transition to the long time behavior is controlled by two processes: the transition from deterministic to diffusional behavior of a particle which does not interact with other particles and the onset of the single-file behavior. If the onset of these processes occurs at different time scales, one would expect an extended region with $\langle z^2\rangle \propto t$ [26]. However, in the considered case, the transition times for both processes are of the same order

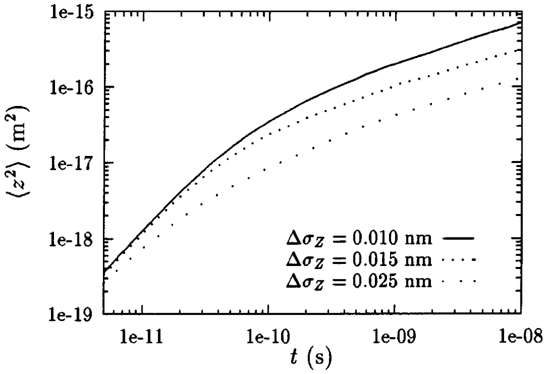

FIG. 2. Mean square displacement of CF_4 in a model single-file system with three different amplitudes $\Delta\sigma_Z$ at 180 K as a function of the observation time at a relative occupancy $\theta = 0.11$ (corresponding to 0.2 molecule per unit cell) obtained by MD simulation.

of magnitude, and there is a continuous transition in the time behavior to the final dependence.

It is noteworthy that already this simple approximation for the zeolite potential yields not only the predicted time dependence but also a mobility factor F of the same order of magnitude as found in the experiments. The mobility factors obtained in the simulation are $F = 3.5 \times 10^{-12}$, 1.6×10^{-12}, and $0.7 \times 10^{-12}\ \mathrm{m^2\,s^{-1/2}}$ (with decreasing mobility factor F for increasing amplitude $\Delta\sigma_Z$), and the free-particle diffusion coefficients D calculated from them via Eq. (5) are 2.8×10^{-6}, 0.6×10^{-6}, and $0.1 \times 10^{-6}\ \mathrm{m^2\,s^{-1}}$. The obtained results compare well with the measured value of $F = 1.5 \times 10^{-12}\ \mathrm{m^2\ s^{-1/2}}$ presented in Table I, and even the smallest simulated value for the mobility F yields a diffusivity D for infinite dilution which is much larger than the experimental values found in zeolites with three-dimensional channel structure. The high translational mobility of noninteracting molecules in $AlPO_4$-5 as resulting from an analysis of the PFG NMR data on the basis of Eq. (5) is thus completely confirmed by the MD simulations.

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