Deviations from the Normal Time Regime of Single-File Diffusion

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Deviations from the ideal single-file behavior in actual systems, such as zeolitic host−guest systems with a one-dimensional channel structure, may occur if (i) there is a possibility of mutual passages of the diffusants and (ii) the influence of the file boundary on the movement of the diffusants cannot be neglected. The conditions under which such deviations may become relevant are investigated both by analytical methods and molecular dynamics simulations. The consequences of these deviations for experimental studies of single-file diffusion are discussed.

I. Introduction

Although during the last couple of years single-file diffusion i.e., the one-dimensional transport of random walkers, which are unable to pass each other, has been considered in numerous theoretical studies,[1−7] only very recently has it become the subject of experimental investigation.[8−13] The experimental evidence for the occurence of single-file diffusion as provided by different research groups, however, is still contradictory. While in refs 10−12, CH_4 in both $AlPO_4$-5 and mordenite was found, for examle, by the PFG NMR technique, to be subjected to single-file diffusion, methane diffusion in $AlPO_4$-5 was found to proceed completely normally by PFG NMR studies communicated in ref 8. For ethane in $AlPO_4$-5, however, unequivocal indications of single-file diffusion were observed by the same authors.[9] Most recent diffusion studies by quasielastic neutron scattering (QENS) were also found to be in contrast with this finding: both methane and ethane diffusion in $AlPO_4$-5 appeared to proceed in the normal way.[13]

As an explanation for the diverging messages, one may consider the possibility that the conditions essential for the observation of genuine single-file diffusion are differently caused in the experiments. These conditions need in particular two requirements: (i) single-file diffusion can only be observed in a time interval where mutual encounters between adjacent molecules occur frequently enough to guarantee a correlated movement of the diffusants, while passages between them are still rare enough (or even nonexistent at all) so that molecular displacement is definitely controlled by single-file behavior (rather than by particle exchange). (ii) Owing to the high degree of correlated motion within single-file systems, for finite file lengths (and this is clearly the case in real physical objects) the microphysical situation at the margins of the individual channels (files) may substantially influence the observed molecular displacement. It must be assumed, therefore, that the single-file systems are large enough so that the boundary conditions (e.g., total blockage or free exchange with the surrounding atmosphere as the two limiting cases) have no influence on the majority of the observed particles.

It is the aim of this contribution to study quantitatively how the observed time dependence of particle propagation of single-file character may be affected by these two influences. We shall in particular consider the cases of mutual passages (section III), totally blocked single files (section IV), and single-file systems in fast exchange with the surrounding atmosphere (section V). Section VI is mainly concerned with the discussion of the obtained theoretical results in relation to the interpretation of experimental data. The subsequent section II is intended to provide a summary of the basic relations of single-file diffusion and of what we understand under its normal time regime.

II. Normal Time Regime of Single-File Diffusion

The term single-file diffusion denotes the movement of particles in a narrow tube, where due to steric restrictions passing of the particles is forbidden. Therefore, the relative order of the particles is conserved. In the case of hard particles, this happens if the particle diameter d_P is greater than half the tube diameter d_T.

A single particle in the tube not in contact with other particles is assumed to undergo normal diffusion with

$$\langle z^2 \rangle_1 = 2D_1 t \tag{1}$$

where D_1 denotes the single-file diffusion coefficient. In this paper we restrict ourselves to this case, although other cases are possible (e.g., deterministic motion of a single particle with $z = vt$, where v denotes the velocity).

For the case where a single particle undergoes normal diffusion, the time behavior in a single-file system of infinite length is known to be[1]

$$\langle z^2 \rangle_{sf} = 2F\sqrt{t} \tag{2}$$

where F denotes the single-file mobility. This quantity is the counterpart of the diffusion coefficient D in normal diffusion.

The single-file mobility can be expressed in terms of the diffusion coefficient D_1 of a single particle as[6,7]

$$F = \frac{1-\theta}{\theta} d_P \sqrt{\frac{D_1}{\pi}} = l\sqrt{\frac{D_1}{\pi}} \tag{3}$$

where

$$l = a - d_P = \frac{1-\theta}{\theta} d_P \tag{4}$$

denotes the clearance or the mean free path between two

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adjacent particles. a is the mean distance between the centers of adjacent particles.

III. Influence of Particle Passing

In a system where the particle diameter is about half the tube diameter $d_P \approx d_T/2$, occasional passages between the particles are possible so that the order of the particles is no longer conserved. If these passages occur at a low rate, the influence on the mean square displacement at short times can be expected to be small.

The process of consecutive particle passages may be interpreted as a random walk process. Let us assume that the average time difference τ between two subsequent passages of the same particle is long compared with the mean time that elapses between the encounters of a particle with the two neighboring ones. This supposition is clearly fulfilled if the probability of mutual passages is sufficiently small. In this case, the passing events are independent of each other.

The average distance by which a particle is shifted as a consequence of a single passing event is the mean distance a between adjacent particles. The total mean square displacement in a random walk process with independent elementary displacements of length a and time intervals τ between them is known to be.[16,19]

$$\langle z^2\rangle_{rw} = \frac{a^2}{\tau}t \tag{5}$$

By comparison with eq 1, from this relation molecular propagation is found to be subjected to normal diffusion with a diffusivity

$$D_{rw} = \frac{a^2}{2\tau} \tag{6}$$

This process of translational propagation with a mean square displacement being proportional to the observation time will occur in addition to the single-file process where the mean square displacement is proportional to the square root of time. Therefore, for sufficiently long times, the process of particle passage will dominate and the mean square displacement in the system eventually increases in proportion to the observation time t, while at short times the influence of particle passages is still small and the time behavior is dominated by the single-file process. Let us denote the transition time between single-file behavior and normal diffusion due to particle passages by t_c. This transition will occur when the mean square displacement due to particle passings $\langle z^2\rangle_{rw}$ becomes equal to the mean square displacement due to single-file diffusion $\langle z^2\rangle_{sf}$:

$$\langle z^2(t_c)\rangle_{rw} = \langle z^2(t_c)\rangle_{sf} \tag{7}$$

Inserting eqs 2, 5, and 6 into eq 7, one obtains for the transition time

$$t_c = \frac{F^2}{D_{rw}^2} \tag{8}$$

This relation holds not only for the case of particle passages but also for any process where the system behavior changes from single-file to normal diffusion.

A system as described above (i.e., with particle diameters $d_P \approx d_T/2$ and rare passing events) was considered in a molecular dynamics simulation. The interaction between the particles was simulated by a Lennard-Jones 12-6 potential with a particle diameter of $\sigma_P = d_P = 0.383$ nm and a strength of $\epsilon = 164k_B$. These quantities correspond to the parameter set usually used for tetrafluoromethane (CF_4). The interaction between the particles and the tube was simulated by an inverse Lennard-Jones potential

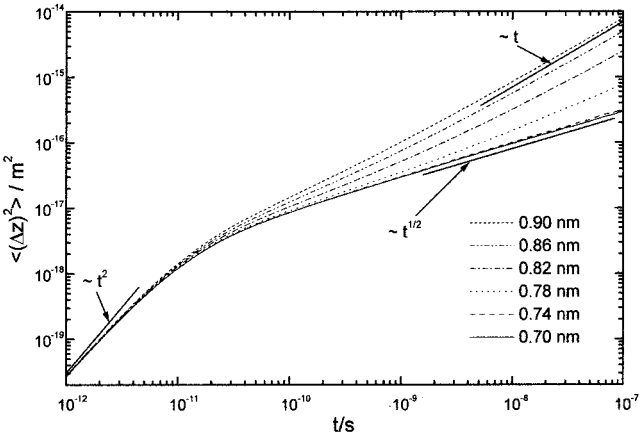

Figure 1. Mean square displacement as a function of the observation time determined by molecular dynamics simulation for different channel diameters.

$$V_T = 4\epsilon\left[\left(\frac{\rho}{\sigma_T}\right)^{12} - \left(\frac{\rho}{\sigma_T}\right)^{6}\right] \tag{9}$$

where ρ denotes the distance between the tube axis and the center of the particles. The potential is cut off at $\rho = \rho_c = \sigma_T/\sqrt[6]{2}$, where the potential has its minimum. The parameter σ_T and the tube diameter d_T are related to each other by

$$d_T = 2\sigma_T + d_P \tag{10}$$

With these potentials the motion of a single particle, which is not in contact with other particles, would be strongly deterministic. Following the procedure described in ref 7, diffusional behavior was attained by introducing a random force. By this random force, the velocities of all particles were statistically changed about once per 10^{-13} s by a factor of about 20%. As a consequence of the action of this random force, a single noninteracting particle was found to follow normal diffusion after an initial ballistic phase. The transition time between ballistic behavior and normal diffusion was found to be $t_t = 10^{-11}$ s. Further details about the simulation procedure and the random force may be found in ref 7.

In the present simulation we used a system of 10 000 particles with diameters $d_P = 0.383$ nm in tubes with diameters d_T in the range of 0.70−0.90 nm. The relative occupancy was chosen to be $\theta = 0.2$ leading to an average distance between particle centers of $a = 1.915$ nm. The mean square displacement as a function of the observation time is given in Figure 1. No deviation from the single-file behavior $\langle z^2\rangle \propto \sqrt{t}$ is seen for the tube diameters $d_T = 0.70$ and 0.74 nm. For both diameters the single-file mobility is found to be $F = 4.5 \times 10^{-13}$ m^2 s$^{-1/2}$. Mean square displacement and mobility are the same in both cases. This finding confirms the result of ref 7 where the tube diameter was found not to influence the motion of the particles along the tube as long as there was pure single-file diffusion. For the larger tube diameters, the mean square displacements show a clear deviation from the $\sqrt{t}$-behavior and tend to be proportional to the observation time t for the largest observation times. Thus, the expected behavior due to particle passages

TABLE 1: Mean Time between Particle Passages (τ), Diffusivities Obtained from Equation 6 (D_{rw}) and from Equation 11 (D_{z^2}), and Transition Time t_c for Different Values of the Channel Diameter d_T

d_T/nm	τ/s	D_{rw}/(m^2 s^{-1})	D_{z^2}/(m^2 s^{-1})	t_c/s
0.70	7.0×10^{-6}	2.6×10^{-13}		3.0
0.74	9.8×10^{-8}	1.9×10^{-11}		5.6×10^{-4}
0.78	5.8×10^{-9}	3.2×10^{-10}		1.6×10^{-6}
0.82	1.5×10^{-10}	1.2×10^{-8}	1.2×10^{-8}	1.3×10^{-9}
0.86	7.1×10^{-11}	2.6×10^{-8}	2.5×10^{-8}	3.0×10^{-10}
0.90	4.5×10^{-11}	4.1×10^{-8}	4.0×10^{-8}	1.2×10^{-10}

does indeed result from the simulation. For comparison with the analytical consideration leading to eqs 5 and 6, the number of particle passages in the simulations has been counted, from which the mean time τ between consecutive passages of a particle could be determined. The results are given in Table 1. Inserting these jump times τ and the average distance a between particles into eq 6 yields the diffusion coefficient D_{rw} due to the passing of particles. For the systems with tube diameters $d_T \geq 0.82$ nm, the diffusion coefficient can be directly determined from the time behavior of the mean square displacement in the simulation. This diffusion coefficient is denoted by D_{z^2} and is simply calculated by

$$D_{z^2} = \frac{\langle z^2(t)\rangle}{2t} \tag{11}$$

at the highest available observation time $t = 10^{-7}$ s. Both diffusion coefficients D_{rw} and D_{z^2} are given in Table 1. The agreement between them is very close.

From the diffusion coefficient D_{rw}, which is available for all diameters and the mobility $F = 4.5 \times 10^{-13}$ m^2 s$^{-1/2}$, which is assumed to be the same for all systems, one can calculate the transition time t_c from single file to normal diffusion. These times are also given in Table 1. For the cases where the transition occurs at the time scale observed in the simulation, the calculated transition times t_c have the correct order of magnitude as may be seen from Figure 1.

It is remarkable that the transition time varies over 10 orders of magnitude while the tube diameter is varied only slightly around $2d_P$. One has to conclude, therefore, that, in the case of particles passing one another, very small changes of the system, either in the real world or in the simulation, can cause a dramatic change in the system behavior. This complication in the analysis of MD simulations in the "transitional" mode between single file and ordinary diffusion has already been noted in refs 14 and 15.

IV. Finite Single-File System with Blocked Boundaries

Proportionality between the mean square displacement and the square root of the observation time as reflected by eq 2 strictly results only from single-file systems of infinite extension. As soon as boundary conditions become relevant, substantial deviations may occur. In single-file systems with closed ends, the mean square displacement will obviously deviate from this dependence approaching a constant value for sufficiently large observation times. Under the assumption that the particles are pointlike and that, except for the preserved particle sequence, there is no correlation between the positions of the diffusants at the beginning and at the end of the experiment, the final value of the mean square displacement of the ith particle may be written as

$$\langle z_i^2\rangle_\infty = \frac{1}{w}\frac{1}{w'}\int_0^L \mathrm{d}x_n \int_0^{x_n}\mathrm{d}x_{n-1}\ldots \int_0^{x_2}\mathrm{d}x_1 \int_0^L \mathrm{d}y_n \int_0^{y_n}\mathrm{d}y_{n-1}\ldots \int_0^{y_2}\mathrm{d}y_1 (y_i - x_i)^2 \tag{12}$$

where x_i and y_i denote the position of the ith particle at $t = 0$ and $t \rightarrow \infty$, respectively. The weight w is found to be

$$w = \int_0^L \mathrm{d}x_n \int_0^{x_n}\mathrm{d}x_{n-1}\ldots \int_0^{x_2}\mathrm{d}x_1 = \frac{L^n}{n!} \tag{13}$$

Calculating the integrals in eq 12 yields

$$\langle z^2{}_i\rangle_\infty = \frac{2L^2}{n+1}\frac{i(n+1) - i^2}{(n+1)(n+2)} \tag{14}$$

and the mean square displacement of the complete system is found as the average over all n particles to be

$$\langle z^2\rangle_\infty = \frac{1}{n}\sum_{i=1}^{n}\langle z_i^2\rangle_\infty = \frac{L^2}{3(n+1)} \approx \frac{L^2}{3n} \tag{15}$$

The solution for particles with finite diameters d_P may be found by replacing the file length L by $L(1 - \theta)$,[6] where $\theta = nd_P/L$ is the relative occupancy. Then, the final result for the mean square displacement is

$$\langle z^2\rangle_\infty = \frac{1}{3}\frac{(1-\theta)^2L^2}{n} = \frac{1}{3}\frac{(1-\theta)^2}{\theta}Ld_P \tag{16}$$

Using eqs 3, 4, and 16, the transition time t_c, which is defined by the relation $\langle z^2\rangle_\infty = 2Ft_c$, is found to be

$$t_c = \frac{\pi}{36}\frac{(1-\theta)^2L^2}{D_1} \tag{17}$$

Note that the value for $\langle z^2\rangle_\infty$ (eq 16) is much smaller than the corresponding value for restricted normal diffusion in one direction,[17] $\langle z^2\rangle\infty = L^2/6$, since during normal diffusion molecules will eventually be distributed over the whole extension L of the crystal, while a single-file particle is already confined by its two neighbors. The risk that the observed molecular mean square displacement is reduced by blockage of the crystallite surface is therefore much larger in single-file systems than in the case of normal diffusion.

V. Single-File Systems with Free Particle Exchange at the File Boundaries

In the case of ordinary diffusion, free particle exchange at the crystallite surface would correspond to the usual boundary condition of dynamic equilibrium between the adsorbed and gaseous phases. If we were unable to distinguish between the individual particles, the evolution of the particle distribution over the single-file system would be unaffected by the mutual confinement of the molecules, since one cannot distinguish whether the individual particles have passed each other or whether they have simply been reflected from each other. This statement is in particular true of the center of gravity, whose position remains unaffected no matter if the molecules are able to pass each other or not. Since in a true single-file system the number of particles on the right and on the left hand side of a given particle remains constant, it is possible to identify the probability distribution of the shift of the center of gravity as an estimate of the probability distribution of the shift of an individual particle.

For the quantitative treatment, we consider a system of random walkers with a particle diameter d_P and a mean time between subsequent jumps τ. The particle diameter is assumed to coincide with the jump length (i.e., the distance between adjacent sites is equal to d_P). Let a system with N particle sites and, therefore, with length $L = Nd_P$ be occupied by n particles leading to a relative occupancy

$$\theta = \frac{n}{N} = \frac{nd_P}{L} \tag{18}$$

A single random walker not restricted by other particles undergoes $m = t/\tau$ jumps in a time interval of length t leading to a mean square displacement of

$$\sigma_1^2 = d_P^2 m = 2D_1 t \tag{19}$$

with a single-particle diffusion coefficient of

$$D_1 = \frac{d_P^2}{2\tau} \tag{20}$$

The propagator (i.e., the probability distribution for the displacement of such a random walker) is well-known to have a Gaussian shape[16]

$$P_1(z,t) = \frac{1}{\sqrt{2\pi}\sigma_1} \exp\left(-\frac{z^2}{2\sigma_1^2}\right) \tag{21}$$

Now, we consider a system of n random walkers and calculate the time behavior of the center of mass for these random walkers. The center of mass is determined by the distribution of particles over the tube. As noted above, any mutual exchange (reordering) of the particles does not change the center of mass.

The shift of the center of mass is found from the average of the shifts of the individual particles. We can consider the shift of an individual particle as a random value chosen from a Gaussian probability density (eq 21) with the width σ_1. From mathematical statistics it is well-known that the average of n random values chosen from a Gaussian density with width σ_1 has again a Gaussian density, where the width of this function is known to be

$$\sigma_n = \frac{\sigma_1}{\sqrt{n}} = \frac{d_P\sqrt{m}}{\sqrt{n}} \tag{22}$$

Therefore, eq 22 represents the width of the propagator of the average of the shifts of the n particles (i.e., the shift of the center of mass of these particles).

Up to now, we have neglected the mutual restrictions of the particles. If the motion of a random walker is restricted by other particles, not every attempt to jump is successful. Because a jump destination is occupied by another particle with probability

$$\frac{n-1}{N-1} \approx \frac{n}{N} = \theta \tag{23}$$

only $m(1-\theta)$ jumps are successful, instead of m. Therefore, the width σ_n for the shift of the center of mass has to be corrected by replacing m by $m(1-\theta)$ leading to

$$\hat{\sigma}_n = \frac{d_P\sqrt{m(1-\theta)}}{\sqrt{n}} \tag{24}$$

for the shift of the center of mass.

In the previous discussion we have not used the essential feature of conservation of the order of the particles. However, as explained above for the calculation of the behavior of the center of mass, it makes no difference whether or not the particles may change their order. The behavior of the center of mass is fully defined by the number of particles and the number of successful jumps regardless of which individual particle undergoes a jump.

On the other hand, the conserved order of the particles does allow the shift of the center of mass to be identified with the shift of an individual particle, at least for long observation times. Assuming that the particles are statistically equally distributed over the tube and that the order of particles is conserved, a shift z of the center of mass necessitates a shift of all particles in the same direction and of the same order of magnitude. Thus, we can identify the motion of the center of mass and the motion of individual particles and, therefore, the mean square displacement of the particles due the shift of the center of mass is

$$\langle z^2 \rangle = \hat{\sigma}_n^2 = \frac{d_P^2 m(1-\theta)}{n} \tag{25}$$

The diffusion coefficient D_{cm} due to the motion of the center of mass is then found to be

$$D_{cm} = \frac{d_P^2(1-\theta)}{2n\tau} \tag{26}$$

$$= \frac{d_P^3(1-\theta)}{2\tau\theta L} \tag{27}$$

$$= D_1\frac{(1-\theta)}{\theta N} \tag{28}$$

The diffusion coefficient D_{cm} of the center of mass is thus related to the diffusion coefficient D_1 of an individual random walker. D_{cm} increases with decreasing relative occupancy θ, reaching D_1 for the case of $\theta = 1/N$, when only one particle resides in the channel. (Note that for very small occupancies the term $1-\theta$ must be replaced by the exact value $1-(n-1)/(N-1)$ according to eq 23).

Equation 28 includes the relation

$$D_{cm} = D_1\frac{(1-\theta)}{N} \tag{29}$$

for the special case of very large relative occupancy (θ chosen such that $(1-\theta)N \ll 1$, i.e., $\theta \rightarrow 1$) derived by H. Rickert.[18]

Molecular propagation due to the shift of the center of mass is superimposed on the single-file mechanism. Since molecular displacements due to the single-file diffusion are only proportional to the square root of time, for long observation times the shift due to the motion of the center of mass dominates. Thus, for sufficiently large t ($t \gg t_c$, see eq 8), the mean square displacement becomes proportional to the observation time t. Using eqs 3 and 8, the transition time is found to be

$$t_c = \frac{L^2}{\pi D_1} \tag{30}$$

and the mean square displacement after the cross-over time t_c becomes

$$\langle z^2 \rangle_c = \frac{2}{\pi} \frac{1-\theta}{\theta} L d_p \tag{31}$$

VI. Discussion

Equations 16 and 31 represent crucial relations for the unambigous measurement of "genuine" single-file displacements in single-file systems of finite extension. In the case of molecular diffusion in obstructed channels, eq 16 yields the maximum mean displacement (i.e., the displacement eventually attained after sufficiently long observation times), where L stands for the channel length between the obstructions. In order to guarantee that the measurements are unaffected by obstructions, the observed displacement must obviously be much smaller than the value indicated by eq 16. Assuming realistic ranges for the average distance between obstructions (L_b = 10...100 μm), the diffusion coefficient of a single particle (D_1 = 10^{-7}...10^{-5} m^2 s^{-1} [11]) and the particle diameter (d_P = 0.4 nm), the transition time to a constant mean square displacement would be in the range of $t_c \approx (1-\theta)^2 \times 10^{-6}$...$10^{-2}$ s with corresponding mean square displacements of $\langle z^2 \rangle_\infty \approx (1-\theta)^2/\theta \times 10^{-15}$...$10^{-14}$ m^2.

These are ranges readily accessible in PFG NMR measurements.[16,17] For the systems so far investigated by this technique,[9−12] the displacements were found to exceed these values significantly. Moreover, in the vast majority of the cases, molecular displacements were found to increase continuously with increasing observation time. Any dominating influence of channel obstruction on the measured single-file diffusivities may therefore be excluded.

In the other limiting case of fast molecular exchange at the file boundaries, molecular displacements of the order of the value given by eq 31 would indicate that there should be a crossover in the time regime from the genuine single-file pattern ($\langle z^2 \rangle \propto \sqrt{t}$, eq 2, for smaller displacements) to the pattern of normal diffusion ($\langle z^2 \rangle \propto t$, eq 1 for larger displacements). Using the same numbers as just considered for the case of restricted diffusion, the corresponding values for the cross-over time and the cross-over mean square displacement are $t_c \approx (1/\pi)10^{-5}$...$10^{-1}$ s and $\langle z^2 \rangle_\infty \approx 2.5(1-\theta)/\theta \times 10^{-15}$...$10^{-14}$ m^2, respectively. These data are again well within the range accessible by PFG NMR. It is a striking feature of the literature data[8−12] that so far such a crossover in the time dependence has not yet been deduced from the PFG NMR measurements. In some cases, one-dimensional propagation in zeolites has been found to follow normal diffusion[8] and it has followed single-file diffusion in other cases,[9−12] but in no case has sufficient experimental evidence for a transition between these two cases been provided. There are several reasons which might explain the lack of experimental evidence for this transition. In order to obtain reliable evidence of the occurence of single-file diffusion, the PFG NMR studies reported in refs 9 and 11 and 12 have been carried out with zeolite crystallites with dimensions up to about L = 200 μm. The cross-over displacements in these cases are at the upper end of the above estimated range, yielding ranges of micrometers. PFG NMR measurements under such conditions are subjected to the largest errors as a consequence of the spin-echo attenuation by T_1 relaxation.[12,16,17] Any deviation from the time regime of single-file diffusion, $\langle z^2 \rangle \propto \sqrt{t}$, was difficult to be detected, therefore. Moreover, eq 31 is clearly only valid in the limiting case of fast molecular exchange at the boundaries. In reality, of course, there is no reason for a certain rate of exchange, and depending on the nature of the channel mouths and the diffusants under study, any rate between infinity and zero should be possible. In the first case, for displacements beyond the cross-over value as given by eq 31, the time dependence of molecular displacement will deviate from the ideal case of single-file diffusion to normal diffusion, (i.e., to larger time exponents attaining eventually proportionality between the mean square displacement and the observation time). In the latter case, with increasing displacements, the time-dependence of single-file diffusion will deviate to smaller time exponents, attaining a final value of zero and a limiting displacement as given by eq 16. The influence of boundaries with medium particle exchange on molecular propagation in single-file systems of finite extension is a problem that is far from being solved (cf, e.g., refs 3, 20, and 21). In any case, the time dependence of molecular displacement must be expected to be intermediate between the two limiting cases. This would mean that the conditions for the measurement of genuine single-file diffusion are in fact less stringent than those resulting from eqs 16 and 31 for the limiting cases of complete obstruction and rapid particle exchange.

Similarly as in the case of rapid particle exchange at the file boundaries, also the mutual passage of molecules within the file should lead to an eventual transition from single-file type molecular propagation (eq 2) to normal diffusion (eq 1).

The channel and particle diameters of the systems under experimental consideration (such as CH_4, C_2H_6, or CF_4 in $AlPO_4$-5[8−12]) are of such an order of magnitude that mutual passages cannot be excluded.[14,15] Additionally, imperfections in the crystal structure where the channel diameter is slightly enlarged may lead to a further possibility of mutual particle passages. The present molecular dynamics simulation (Figure 1) has shown that even small changes of the simulation parameters may have dramatic consequences on the time dependence of the molecular mean square displacement. Although of the same type, the zeolite specimens may differ in subtle structural details as a consequence of different synthesis or pretreatment procedure, which thus turn out to be possibly of crucial importance for the propagation pattern of the guest molecules. These differences may be caused by differences in the rate of mutual passing of the particles within the channels as well as of particle exchange at the file boundaries. Hence even identical experimental techniques, such as PFG NMR, may lead to different conclusions if not applied to the identical sample. The situation is far more complicated if different experimental techniques are applied, since in such cases quite different ranges of observation time may be covered. While quasielastic neutron scattering (QENS) is capable of tracing the transition between the ballistic phase, an intermediate state of normal diffusion and single-file diffusion (cf. the time scale between 10^{-13} and 10^{-9} s in Figure 1),[13,22] PFG NMR covers the range of observation times between 10^{-1} and 1 s.[16,17] It is quite possible, therefore, that these two techniques trace completely different diffusional regimes, where—owing to the relavant range of observation times—PFG NMR is more likely to trace single-file diffusion than QENS. In contrast to both PFG NMR and QENS, the zero length column (ZLC) tracer exchange method[23] monitors the net effect of particle exchange with the surroundings rather than the mean molecular displacement within the single-file system. The range of observation times is typically of the order of seconds or larger, notably

exceeding that of PFG NMR. It is not unexpected, therefore, that measurements by this technique are able to cover the regime of dominating mutual particle passages as claimed in ref 24, while the PFG NMR data are still controlled by single-file diffusion.

VII. Conclusion

The time dependence of the mean square molecular displacement as a crucial experimental dependency for identifying single-file diffusion in zeolites with one-dimensional channel pores is found to depend decisively on the nature of the system under study. Deviations from ideal single-file behavior i.e., from proportionality between the mean square displacement and the square root of the observation time occur as soon as the finite length of the single-file system must be taken into consideration and the rate of mutual passages of the particles within the single-file system cannot be considered anymore to be negligibly small. Both influences are considered quantitatively by analytical means and, in the latter case, by molecular dynamics simulations. Both the nature of the system and the range of observation times accessible by the experimental technique turn out to be of decisive influence on the observed time regime. Owing to the range of observation times accessible by this technique, the potentials of PFG NMR for identifying single-file diffusion in zeolites are found to be superior to those of other diffusion techniques like QENS or the ZLC tracer exchange method.

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