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Propagator and mean-square displacement in single-file systems

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Abstract. It is shown that the propagator in single-file systems may quite generally be deduced from the propagator in the corresponding unrestricted case. Irrespective of its structure in the unrestricted case, the propagator of single-file systems in the long-time limit approaches a Gaussian distribution. It is found that the exponent of the time dependence of the mean-square displacement is reduced by a factor of two, compared with the unrestricted case. Examples for different models of particle propagation are considered and compared with literature data. For one model the theoretical result is compared with a molecular dynamics simulation.

One-dimensional arrays of particles, where the individual particles are not allowed to change the order of their arrangement are generally referred to as single-file systems. Consequently, a particular particle in a single-file system will permanently remain between the same neighbours. The displacement of a given particle over a long distance will therefore necessitate the shift of many other particles into the same direction, leading to a high degree of mutual correlation between the movement of different particles. This correlation substantially complicates the description of the dynamic behaviour of single-file systems and has made them a challenging topic of both fundamental research [1–3] and applied studies [4–6].

A realization of a single-file system should occur in some types of zeolites, e.g. Mordenite, ZSM-12, or $\text{AlPO}_4\text{-5}$. These zeolites have a one-dimensional pore structure with such diameters that molecules diffusing in these pores cannot pass each other. This situation should lead to single-file behaviour of the diffusing particles. Due to the catalytic capabilities of zeolites there is a considerable interest in investigating the transport properties of molecules in zeolites. The effectivity of catalytic reactions does not depend only on the reaction rate in the zeolite but also on the availability of the reaction products outside the zeolite. This, however, depends strongly on the transport and diffusion behaviour of the molecules.

Single-file systems have so far generally been assumed to contain random walkers. The exclusion of mutual passages of the random walkers in single-file systems has been shown to lead to a mean-square displacement which is proportional to the square root of the observation time [1–3] rather than to the observation time itself, as in the case of unrestricted walkers.

Generally, the dynamic behaviour of multi-particle systems is represented in terms of the so-called propagator $P(z, t)$, i.e. the probability density that during a time interval t an

arbitrarily selected particle will be shifted over a distance z . In what follows, a method will be presented by which the propagator of a single-file system may easily be derived from the main features of the 'free' propagator, i.e. of the propagator in the unrestricted case. The method applies to random walkers as well as to any other type of particle propagation.

Let us introduce the free propagator $P_f(s, t)$, which describes the motion of non-interacting particles in the given system, i.e. the motion of particles that do not feel the presence of any other particle. $P_f(s, t)$ can be found by investigating the motion of a single particle in the given system. In certain non-ergodic cases, one has additionally to sum or integrate over all initial conditions. Later it will be shown that the particular shape of the free propagator does not play any role for the long-time behaviour of the single-file system. It is only the mean-square displacement and its time dependence which are essential.

For deriving the propagator under single-file conditions, we will first consider the interaction of adjacent point-like particles. Assuming that the two particles interact in the interior of a box and that it is only possible to determine the velocities and instants of time when the particles enter and leave this box, there is no way of determining whether the particles have freely passed each other without any interaction or whether the particles did interact, thus maintaining their relative positions to each other. This means that the spatial distribution of particles after a certain time t is exactly the same for both interacting and non-interacting particles. However, in contrast to the spatial distribution, the order of the particles is different. While non-interacting particles may mutually exchange their positions leading to a complete collapse of the initial order, this order is preserved over all times in the case of interacting particles (see figure 1).

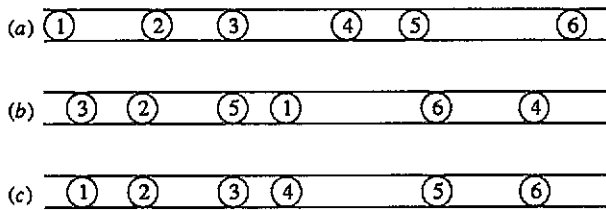


Figure 1. Spatial distribution and particle order for the cases of non-interacting and interacting particles. (a) Initial state at $t = 0$. (b) Final state for non-interacting particles; the particles have changed their order. (c) Final state for interacting particles (single-file behaviour); the order of particles is as in (a) and their spatial distribution as in (b).

This situation can be used to calculate the propagator $P(z, t)$ of the single-file system from the free propagator $P_f(s, t)$, where we shall use the notation z and s to distinguish between shifts in the interacting and non-interacting system. In our derivation of the propagator a positive particle shift z is assumed. Due to symmetry, the relation $P(z, t) = P(-z, t)$ holds and the result for negative shifts is obtained by taking the absolute value $|z|$.

For the calculation it is easier to consider the probability

$$W(z, t) = \int_z^\infty dz' P(z', t) \quad (1)$$

that a particle is shifted over a distance greater than z , than the propagator itself.

To allow a shift of a given particle from the starting point $z_0 = 0$ to the end-point z in a single-file system, all particles initially between z_0 and z must be finally on the right of z . Introducing the probability $w_1(z, n)$ of finding n particles in the region $z_0 \dots z$, and

the probability $w_2(t, k)$ that k particles are shifted from the left of a certain position to the right during t , one may write

$$W(z, t) = \sum_{n=0}^{\infty} w_1(z, n) \sum_{k=n+1}^{\infty} w_2(t, k) \tag{2}$$

where the first sum runs over the number n of particles in $z_0 \dots z$, and the second sum runs over the number k of particles which are on the right of z after time t . $W(z, t)$ does not include the case that the particle does not move, i.e. the shift $z = 0$. This case will be considered separately. It should be noted that, strictly speaking, the probability $w_2(t, k)$ is not independent of n (and z), implying a correlation between w_1 and w_2 . However, it will be shown, that this correlation may be neglected without substantially affecting the final result.

The particles are assumed to be distributed statistically uniformly over the infinite chain with density

$$c = N/L \tag{3}$$

where N is the average number of particles in a region of length L . The probability $w_1(z, n)$ is then given by the Poisson distribution

$$w_1(z, n) = \frac{(c|z|)^n}{n!} e^{-c|z|} . \tag{4}$$

For the determination of the probability $w_2(t, k)$ we make use of the above consideration, that the evolution of the spatial distribution of interacting and non-interacting particles is identical. Hence the number k of particles which are initially on the left of z and finally on the right of z is also the same. The probability $w_2(t, k)$ can therefore be determined using the free propagator of the non-interacting system. Thus, in a manner similar to that in [3], where the treatment of correlated movements in single-file systems was made possible by considering the uncorrelated movement of the 'holes' rather than that of the particles, in the present context we refer the (correlated) particle movement in single-file systems to the uncorrelated movement of non-interacting particles. The net number k of particles propagating to the right of position z during t is obviously equal to the difference $k_r - k_l$ of the numbers of particles which pass z to the right and to the left, respectively. The instants of time at which non-interacting particles are passing a given point follow a statistically uniform distribution, so that the probability $p(t, m)$ that m particles pass z during time t is again given by a Poisson distribution

$$p(t, m) = \frac{b^m}{m!} e^{-b} \tag{5}$$

where b is the average number of particles passing point z during t . The time dependence of $p(t, m)$ is included in that of b .

This quantity b , and with it equation (5), obviously depends on the density of the particles on their starting positions on the left- and right-hand sides of z , respectively. Following the notation of (3), the particle density is equal to n/z in the interval $z_0 \dots z$, while it is equal to the constant value $c = N/L$ [cf equation (3)] elsewhere. It is the specification of the particle density in the interval $z_0 \dots z$ which produces a correlation between the probabilities w_1 and w_2 . For sufficiently large time intervals, however, the majority of the particles passing position z from the left will stem from positions on the left-hand side of z_0 , where the particle density is the same as on the right-hand side of position z . It is therefore justified to use equation (5) with the same value of b for the particles passing z from the left and from the right. The assumption that most of the

particles passing position z are from outside the interval $z_0 \dots z$, is obviously most critical for large intervals z and hence for large mean particle numbers cz . In this case, however, the Poisson distribution will exhibit a sharp maximum near cz , so that again the same probability function $p(t, m)$ may be used for the particles stemming from either side of position z .

The parameter b may be determined by integrating over the probabilities that a particle is found initially on the left of position z and will be found on a position on the right of z after t :

$$b = \int_{-\infty}^z dz' c \int_{z-z'}^{\infty} ds P_t(s, t) = \frac{1}{2} c \langle |s| \rangle \tag{6}$$

where $\langle |s| \rangle = \int_{-\infty}^{\infty} ds |s| P_t(s, t)$ denotes the mean absolute shift of a non-interacting particle.

With the function $p(t, m)$ thus determined, the probability $w_2(t, k = k_r - k_l)$ becomes

$$w_2(t, k) = \sum_{k_1=0}^{\infty} p(t, k_1) p(t, k_1 + k) = I_k(2b) e^{-2b} \tag{7}$$

where the I_k are the modified Bessel functions [7].

Inserting equations (4) and (7) into (2), by using equation (1) one obtains

$$\tilde{P}(z, t) = - \sum_{n=0}^{\infty} c \frac{(c|z|)^{n-1}}{n!} (n - c|z|) \sum_{k=n+1}^{\infty} I_k(2b) e^{-c|z|-2b} \tag{8}$$

where $\tilde{P}(z, t)$ denotes the propagator at $z \neq 0$. Some simple reordering and index shifting result in

$$\tilde{P}(z, t) = \sum_{n=0}^{\infty} \frac{(c|z|)^n}{n!} \sum_{k=n+1}^{\infty} [I_k(2b) - I_{k+1}(2b)] ce^{-c|z|-2b}. \tag{9}$$

The sum over the Bessel functions can be simplified as

$$\sum_{k=n+1}^{\infty} (I_k - I_{k+1}) = \lim_{m \rightarrow \infty} (I_{n+1} - I_m) = I_{n+1} \tag{10}$$

and thus one obtains for the propagator

$$\tilde{P}(z, t) = \sum_{n=0}^{\infty} \frac{(c|z|)^n}{n!} I_{n+1}(2b) ce^{-c|z|-2b}. \tag{11}$$

The infinite sum can be solved analytically [8] and the propagator is found to be

$$\tilde{P}(z, t) = ce^{-c|z|-2b} \left(\frac{c|z|}{b} + 1 \right)^{-\frac{1}{2}} I_1 \left((4b^2 + 4c|z|b)^{\frac{1}{2}} \right). \tag{12}$$

As mentioned in connection with equation (2), the function $\tilde{P}(z, t)$ thus determined does not include the case that the particle remains at $z = 0$. In this case the numbers of particles passing the position $z = 0$ from the left and from the right are the same. According to (7) the probability for that case is

$$w_2(t, 0) = I_0(2b) e^{-2b}. \tag{13}$$

The complete propagator is therefore given by

$$P(z, t) = \sum_{n=0}^{\infty} \frac{(c|z|)^n}{n!} I_{n+1}(2b) ce^{-c|z|-2b} + I_0(2b) e^{-2b} \delta(z) \tag{14}$$

where the Dirac delta function $\delta(z)$ has been included because the term $I_0(2b)e^{-2b}$ applies only to $z = 0$. As it should be, the propagator is normalized, i.e. $\int_{-\infty}^{+\infty} dz P(z, t) = 1$, and $P(z, 0) = \delta(z)$.

The mean-square displacement (being identical with the second moment) is defined as

$$\langle z^2 \rangle = a \int_{-\infty}^{\infty} dz z^2 P(z, t). \tag{15}$$

Inserting equation (14) one obtains

$$\begin{aligned} \langle z^2 \rangle &= 2ce^{-2b} \sum_{n=0}^{\infty} \frac{I_{n+1}(2b)}{n!} \int_0^{\infty} dz z^2 (c|z|)^n e^{-c|z|} \\ &= 2 \frac{e^{-2b}}{c^2} \sum_{n=0}^{\infty} I_{n+1}(2b) \frac{(n+2)!}{n!} \\ &= \frac{2b}{c^2} \{1 + [I_1(2b) + I_0(2b)]e^{-2b}\}. \end{aligned} \tag{16}$$

For large times t , and hence for large values of b , the Bessel functions behave as

$$I_n(2b) \rightarrow (4\pi b)^{-1/2} e^{2b} \tag{17}$$

so that the mean-square displacement becomes

$$\langle z^2 \rangle = \frac{2b}{c^2}. \tag{18}$$

In the special case of single-file diffusion of random walkers, the propagator for long times has been shown to approach a Gaussian distribution [3]. In what follows it will be demonstrated that this is true for any type of movement in single-file systems. For this purpose, we consider the propagator $\tilde{P}(z, t)$ for $z \neq 0$. For long times, and thus for large b , according to (17) the Bessel functions behave as

$$I_n((4b^2 + 4c|z|b)^{1/2}) \rightarrow (2\pi)^{-1/2} (4b^2 + 4c|z|b)^{-1/4} \exp\left\{(4b^2 + 4c|z|b)^{1/2}\right\} \tag{19}$$

and, inserting this relation into (12), the propagator becomes

$$\begin{aligned} \tilde{P}(z, t) &= ce^{-c|z| - 2b} \left(\frac{c|z|}{b} + 1\right)^{-1/2} (2\pi)^{-1/2} (4b^2 + 4c|z|b)^{-1/4} \exp\left\{(4b^2 + 4c|z|b)^{1/2}\right\} \\ &= c(4\pi b)^{-1/2} \left(\frac{c|z|}{b} + 1\right)^{-3/4} \exp\left\{-c|z| - 2b + (4b^2 + 4c|z|b)^{1/2}\right\}. \end{aligned} \tag{20}$$

Using the Taylor expansion for the square root in the exponent

$$(4b^2 + 4c|z|b)^{1/2} = 2b \left(1 + \frac{1}{2} \frac{c|z|}{b} - \frac{1}{8} \left(\frac{c|z|}{b}\right)^2 + \frac{1}{16} \left(\frac{c|z|}{b}\right)^3 \dots\right) \tag{21}$$

one obtains for the propagator

$$\tilde{P}(z, t) = c(4\pi b)^{-1/2} \left(\frac{c|z|}{b} + 1\right)^{-3/4} \exp\left\{-\frac{c^2}{4b} z^2 + \frac{c^3}{8b^2} z^3 \dots\right\}. \tag{22}$$

In the limit of large b only the leading terms in the sums contribute to the result and substituting the mean-square displacement $\langle z^2 \rangle$ for $2b/c^2$, the propagator in the long-time limit finally becomes

$$\tilde{P}(z, t) = \frac{1}{\sqrt{2\pi \langle z^2 \rangle}} \exp\left\{-\frac{z^2}{2\langle z^2 \rangle}\right\} \tag{23}$$

which is exactly the Gaussian distribution. The second summand in (14), which was added to describe the propagator at $z = 0$ correctly, vanishes for large times t . Thus, independent of the shape of the unrestricted propagator, the propagator of a single-file system is found to approach a Gaussian distribution in the long-time limit.

For particles with non-vanishing radius r the treatment must be modified slightly. Let us again assume that the particles interact in a box of length L_b and that only the velocities and instants of time when the particles are entering or leaving the boxes are known. Now, in contrast to the case of infinitely small particles, it is possible to distinguish between interacting and non-interacting particles: The average distance covered by interacting particles within a box is equal to $L_b - 2r$, while non-interacting particles have to move over the total length L_b . Consequently, the mean lifetimes of the particles within the boxes are different. However, by changing the box length for interacting particles to $L_b + 2r$, the two cases may again be made indistinguishable. From this it follows that the results for a system with particles with radius r may be found from a system with point-like particles by an appropriate change of the length scale. Obviously, the shifts of particles with radius r in a single-file system with N particles per length L_r are the same as the shifts of point-like particles in a system with length

$$L = L_r - 2rN = L_r(1 - \theta) \quad (24)$$

where $\theta = 2rN/L_r$ is the relative amount of space occupied by particles (relative occupancy). The only space-dependent parameters are the quantities b and c . With equation (24) they become

$$c = \frac{N}{L} = \frac{N}{L_r(1 - \theta)} \quad (25)$$

$$b = \frac{1}{2} \frac{N}{L} \langle |s| \rangle = \frac{1}{2} \frac{N}{L_r(1 - \theta)} \langle |s| \rangle. \quad (26)$$

Inserting these relations into (18) yields

$$\langle z^2 \rangle = \frac{2b}{c^2} = (1 - \theta) \frac{\langle |s| \rangle}{c_r} \quad (27)$$

with $c_r = N/L_r$. $(1 - \theta)/c_r$ is simply the clearance between two adjacent particles, which may also be interpreted as the mean free path between succeeding particle encounters. According to (27), the mean-square displacement in single file systems is therefore simply the product of the mean shift of a free (i.e. non-interacting) particle and its mean free path in the case of interaction.

The formalism thus derived will now be used for the treatment of a few special cases. For a random walker with jump length l and time step τ , the free propagator is

$$P_f(s, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left\{ \frac{-s^2}{4Dt} \right\} \quad (28)$$

with $D = l^2/2\tau$ denoting the diffusion coefficient. With equation (28), the mean shift is found to be

$$\langle |s| \rangle = \sqrt{\frac{4D}{\pi}} \sqrt{t}. \quad (29)$$

The particle diameter l , particle concentration c_r , and relative occupancy θ are related to each other by the expression $c_r = \theta/l$. Thus, from (27) one finally obtains

$$\langle z^2 \rangle = \frac{(1 - \theta)}{\theta} l^2 \sqrt{\frac{2}{\tau\pi}} \sqrt{t} \quad (30)$$

which is identical with the result known from the literature [1-3].

Let us now consider an ensemble of hard spheres of radius r which move completely deterministic in a narrow tube. Let the spheres have simply two velocities : v_0 and $-v_0$. The mean displacement for free particles is then

$$\langle |s| \rangle = v_0 t \tag{31}$$

and, via (27), the mean-square displacement in the single-file system becomes

$$\langle z^2 \rangle = (1 - \theta) \frac{\langle |s| \rangle}{c_r} = (1 - \theta) \frac{v_0}{c_r} t. \tag{32}$$

The same result would be obtained for spheres characterized by a Gaussian velocity distribution with the free propagator

$$P_f(s, t) = \frac{1}{\sqrt{2\pi \langle v^2 \rangle t^2}} \exp \left\{ -\frac{s^2}{2 \langle v^2 \rangle t^2} \right\}. \tag{33}$$

The mean absolute shift obtained from this propagator is

$$\langle |s| \rangle = \sqrt{\frac{2 \langle v^2 \rangle}{\pi}} t \tag{34}$$

and, therefore, choosing $\langle v^2 \rangle = (\pi/2)v_0^2$, the mean displacement of the free particles is found to be the same as that given by (31), so that consequently also the single-file propagator and the mean-square displacement are the same as in the case considered previously.

The case of the Gaussian velocity distribution was also investigated by a molecular dynamics simulation. The system was simulated by 5000 particles using the velocity-Verlet method [9, 10] in the microcanonical ensemble. The particle-particle interaction was given by a shifted force Lennard-Jones 12-6 potential

$$V_p(r) = \begin{cases} 4\epsilon_p \left(\left(\frac{\sigma_p}{r} \right)^{12} - \left(\frac{\sigma_p}{r} \right)^6 \right) - c_1(r^2 - r_c^2) - c_2 & \text{for } r < r_c \\ 0 & \text{for } r > r_c. \end{cases} \tag{35}$$

The cut is at $r_c = 2\sigma_p$ and the constants c_1 and c_2 are set to values which ensure that both potential and force vanish at $r = r_c$. The particle diameter is set to $\sigma_p = 0.383$ nm and ϵ_p is set equal to $164k_B$ (k_B denoting the Boltzmann constant). The mass of a particle was chosen to be $m = 83.8$ u (with u denoting the unified atomic mass unit). The interaction between the particles and the tube was simulated by a well potential

$$V_t(\rho, z) = \begin{cases} 4\epsilon_t \left(\left(\frac{\rho}{\sigma_t} \right)^{12} - \left(\frac{\rho}{\sigma_t} \right)^6 \right) + \epsilon_t & \text{for } \rho > \rho_c \\ 0 & \text{for } \rho < \rho_c \end{cases} \tag{36}$$

where $\rho_c = \sigma_t/\sqrt[6]{2}$. ρ denotes the distance between the tube axis and the centre of the particle. The parameters are set to $\sigma_t = 0.12$ nm and $\epsilon_t = 150k_B$. This choice of the parameters ensures that mutual passages of particles could be excluded.

To simulate an infinite tube, periodic boundary conditions in the z -direction are used. This boundary condition effects that with increasing observation time the mean-square displacement approaches a finite value. For a given particle density, this value is proportional to the length of one period, and hence to the number of particles considered. The number of particles in our simulation (5000) was chosen to be large enough so that during the observation time considered such finite-size effects did not influence the simulation results.

The average distance between adjacent particle centres was chosen to be equal to $5\sigma_p$ leading to a particle density $c_r = (5\sigma_p)^{-1}$ and to a relative occupancy $\theta = 0.2$. With this choice the range of interaction ($2\sigma_p$) is short in comparison with the average distance between the particles. Therefore, the theoretical results, which were obtained for particles with a hard interaction potential, should be applicable.

The simulation was done at a temperature of $T = 300$ K which leads to a mean-square displacement in the single-file system of

$$\langle z^2 \rangle = \frac{1 - \theta}{c_r} \sqrt{\frac{2k_B T}{\pi m}} t = 2.11 \times 10^{-7} [\text{m}^2 \text{s}^{-1}] t. \quad (37)$$

A more detailed description of the molecular dynamics simulation together with extensive simulations for a variety of systems is given in a forthcoming paper [11].

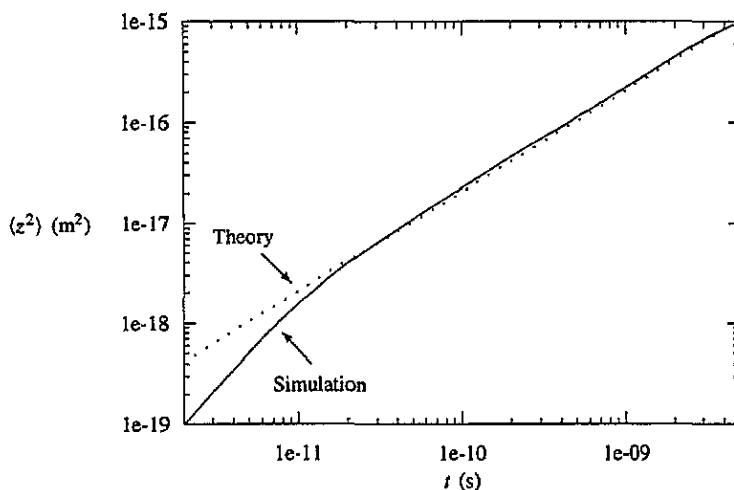


Figure 2. Comparison of theoretical result and molecular dynamics simulation. The statistical errors in the simulation results are very small due to the large number of particles (5000) used in the simulation.

Figure 2 shows the results of the simulation. For times $t > 10^{-11}$ s the theoretical curve and the simulation results are found to be in good agreement. For shorter simulation times the probability for an interaction with the next particle is small and the particles move essentially as free particles. This short-time behaviour is not included in the theoretical consideration given above. The excellent agreement is somewhat surprising because the theoretical result was obtained for an ideal one-dimensional system. The simulation, however, was done in a system where the particles can move in all three directions. Hence, any interaction between two particles is accompanied by a momentum transfer between the radial direction and the z -direction. One has to conclude therefore, that the degrees of freedom in x - and y -direction of molecular motion do not lead to any essential deviation from the ideal one-dimensional case.

It is interesting to note that in the last example the mean-square displacement of the particles in the single-file system is found to be proportional to t rather than to \sqrt{t} , as in the case of a single-file system consisting of random walkers. This, however, is the immediate consequence of the proportionality of $\langle z^2 \rangle$ and $\langle |s| \rangle$. Assuming that the mean-square displacement in the non-interacting system is $\langle s^2 \rangle \propto t^m$ and thus $\langle |s| \rangle \propto t^{m/2}$, the

mean-square displacement in the single-file system becomes $\langle z^2 \rangle \propto \langle |s| \rangle \propto t^{m/2}$. Hence, the exponent of the time dependence of the mean-square displacement is reduced by a factor of two in comparison with the case of non-interacting particles.

It has thus turned out that the time behaviour of a single-file system is exclusively determined by the mode of movement of the individual particles. If a particle moves in a completely random way, e.g. due to a stochastic interaction with the crystal lattice in a zeolite with one-dimensional pore structure, the mean-square displacement of the single-file system becomes proportional to the square root of time. Otherwise, if a particle moves in a completely deterministic way and if a change of the velocity is only possible due to interaction with other particles of the same kind, the mean-square displacement becomes proportional to t . If the forces acting on a particle and leading to the random motion are small, then, at a certain time scale, there will be a transition from deterministic to random behaviour. At this time scale the exponent of the time dependence of the mean-square displacement in the single-file system will change from 1 to $\frac{1}{2}$.

Table 1. The time behaviour of the mean-square displacements $\langle z^2 \rangle$ in the case of one-dimensional single-file diffusion and of ordinary diffusion. In the case of single-file diffusion the time behaviour depends on the behaviour of a single, isolated particle, while the time dependence during ordinary diffusion is independent of the mode of motion of individual particles. $\langle |s| \rangle$ denotes the mean absolute shift of a single non-interacting particle.

Single particle $\langle s \rangle$	Single-file diffusion $\langle z^2 \rangle$	Ordinary diffusion $\langle z^2 \rangle$
$\propto t$	$\propto t$	$\propto t$
$\propto t^{1/2}$	$\propto t^{1/2}$	$\propto t$

Table 1 summarizes the time behaviour of a single file system dependent on the mean absolute shift of a single particle. For comparison, the time behaviour for ordinary (e.g. three-dimensional diffusion) is also included.

In this case, independent of the behaviour of a single particle, the mean-square displacement is proportional to the time t . The deterministic case would be represented, e.g. by a low-density gas, where the atoms move without any change of velocity until they interact with another atom. The case of random motion would be given by a system of Brownian particles in a gas which move randomly due to the influence of the gas molecules and which interact with each other. In both cases the mean-square displacement is clearly proportional to t .

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