Analytical results for the reactivity of a single-file system

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We derive analytical expressions for the reactivity of a single-file system with fast diffusion and particles entering and leaving the system at one end. If the conversion reaction is fast, then the reactivity depends only very weakly on the system size, and the conversion is about 100%. If the reaction is slow, then the reactivity becomes proportional to the system size, the loading, and the reaction rate constant. If the system size increases the reactivity goes to the geometric mean of the reaction rate constant and the rate of particles entering and leaving the system. For large systems, the number of unconverted particles decreases exponentially with distance from the open end.

One-dimensional zeolites, transport of ions in biological membranes, conduction in superionic and organic conductors, neural transmission, and one-dimensional photonic materials are some of the processes and systems that can be regarded as single-file systems (SFS) [1–3]. They are one-dimensional systems with the property that particles cannot pass each other, which leads to very interesting kinetic effects [2]. Research on SFS's has focused on the diffusion, because the mean-square displacement in a SFS is proportional to the square root of time, and is not proportional to time [3–5]. Molecular dynamics [5–7], dynamic Monte Carlo (DMC) [8–10], and reaction-diffusion equations [11] have mainly been used. Few studies have included reactions [10,12,13]. We have argued that this is unfortunate, because if diffusion is fast the temporal dependence of the mean-square displacement is not very relevant, but there are still effects from the non-passing of the particles.

In a previous paper we have investigated steady-state properties of a SFS for different assumptions of the reactive site distribution using DMC as well as analytical techniques [10]. In this paper we derive exact results for the case when all sites are reactive. These results give detailed insight into the relationships of the various system parameters and the reactivity.

Our model consists of S sites forming a one-dimensional finite chain. Each site is numbered consecutively from 1 for the site on one end, to S for the site on the other end. Each site is vacant or is occupied by a particle. We have two types of particles; A and B. An A particle can be converted into a B particle on any site. Particles can only enter at or leave from site 1. Only A's enter, but both A's and B's leave. Both types of particles diffuse by making random hops to neighboring sites if vacant.

The evolution of the system is described by a master equation [14,15]:

$$\frac{dP_\alpha}{dt} = \sum_\beta [W_{\alpha\beta}P_\beta - W_{\beta\alpha}P_\alpha], \qquad (1)$$

where α and β refer to the configuration of the system (a particular distribution of particle over the sites), the P's are the probabilities of the configurations, t is real time, and the W's are constants that give the rates with which reactions change the occupations of the sites. $W_{\alpha\beta}$ corresponds to the reaction that changes β into α. The rate constants in our model are W_{in} for an A entering at site 1 if vacant, W_{out} for a particle leaving from site 1, W_{rx} for the conversion of an A into a B on any site, and W_{diff} for a hop of a particle to a vacant neighboring site.

If the diffusion is infinitely fast, we can derive a simpler master equation for the number of particles in the system:

$$\frac{dP_N}{dt} = W_{in}\left[1 - \frac{N-1}{S}\right]P_{N-1} - W_{in}\left[1 - \frac{N}{S}\right]P_N$$
$$+ W_{out}\frac{N+1}{S}P_{N+1} - W_{out}\frac{N}{S}P_N, \qquad (2)$$

where P_N is the probability that there are N particles in the system. This is a master equation of a one-step Markov process [15].

Let P_{NK} be the solution of Eq. (2) with N being the number of particles and the initial condition; $P_{NK}(0) = \delta_{NK}$. Let Q_{NK} also be a solution with $Q_{NK}(0) = \delta_{NK}$, but now for the master equation with an absorbing boundary at M; i.e., we remove the term in Eq. (2) that corresponds to an A entering when there are M particles in the system. With $N \geqslant M$ we have

$$P_{NK}(t) = Q_{NK}(t) + \int_0^t dt' \, P_{NM}(t-t')f_{MK}(t'), \qquad (3)$$

with $f_{MK}(t)$ being the probability distribution that if at time $t=0$ the number of particles is K, this number becomes M for the first time at time t with $M < K$. This equation is called the renewal equation [15]. If we take $N=M$ in the renewal equation, then we have $Q_{MK}(t)=0$ by definition. So we get the integral equation

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$$P_{MK}(t) = \int_0^t dt' \, P_{MM}(t-t') f_{MK}(t') \qquad (4)$$

for f_{MK}.

The probability distribution for the time that a particle stays in the system is given by $f_{N,N+1}(t)$. The probability that the particle leaves the system without being converted is then

$$\int_0^\infty dt \, \exp(-W_{\mathrm{rx}} t) f_{N,N+1}(t). \qquad (5)$$

This is equal to $\hat{f}_{N,N+1}(W_{\mathrm{rx}})$ with $\hat{f}_{N,N+1}$ being the Laplace transform of $f_{N,N+1}$. The reason for using this Laplace transform is that it is related to the Laplace transform of the solution of the master equation through the renewal equation. Laplace transforming Eq. (4) yields

$$\hat{P}_{MK}(s) = \hat{P}_{MM}(s) \hat{f}_{MK}(s). \qquad (6)$$

If we write the master equation (2) in matrix-vector notation as $\dot{P} = \mathbf{W} P$, and Laplace transform it we get

$$\sum_M (s\delta_{NM} - \mathbf{W}_{NM}) \hat{P}_M(s) = P_N(0). \qquad (7)$$

With the initial condition for P_{MK} this yields

$$\hat{P}_{MK}(s) = [(s-\mathbf{W})^{-1}]_{MK}, \qquad (8)$$

so that

$$\hat{f}_{MK}(s) = \frac{[(s-\mathbf{W})^{-1}]_{MK}}{[(s-\mathbf{W})^{-1}]_{MM}}. \qquad (9)$$

We define the reactivity B_{prod} as the number of particles that is being converted per unit time. To get B_{prod} we have to multiply the probability that a particle is converted by W_{in} and make a weighted average over the number of particles in the system. The probability that a particle is converted equals $1 - \hat{f}_{N,N+1}(W_{\mathrm{rx}})$, and the rate of particles entering equals $W_{\mathrm{in}}(1-N/S)$. At steady state, the number of particles in the system is given by [10]

$$P_N^{(ss)} = \binom{S}{N} \left[\frac{W_{\mathrm{out}}}{W_{\mathrm{in}}+W_{\mathrm{out}}} \right]^S \left[\frac{W_{\mathrm{in}}}{W_{\mathrm{out}}} \right]^N. \qquad (10)$$

Combining this results in

$$B_{\mathrm{prod}} = W_{\mathrm{in}} \sum_{N=0}^{S-1} P_N^{(ss)} \left[1 - \frac{N}{S} \right] [1 - \hat{f}_{N,N+1}(W_{\mathrm{rx}})]. \qquad (11)$$

Note that all these results follow exactly from the master equation (1) for infinitely fast diffusion.

Figure 1 shows the reactivity for two finite system sizes and three loadings. The loading θ is defined as the probability that a site is occupied at steady state. It is equal to [10]
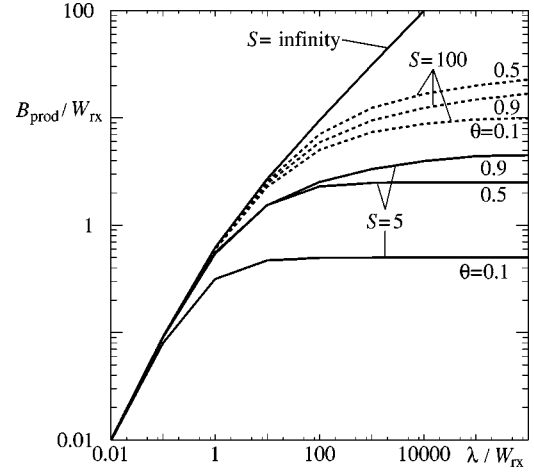

FIG. 1. The reactivity B_{prod} as a function of the rate of particles entering and leaving the system λ. The reactivity and the rate of particles entering and leaving the system are scaled with the rate constant of the conversion W_{rx}. S is the number of sites in the system.

$$\theta = \frac{W_{\mathrm{in}}}{W_{\mathrm{in}}+W_{\mathrm{out}}}. \qquad (12)$$

The reactivity is compared to the (average) rate of particles entering and leaving the system λ, which at steady state is given by

$$\lambda = W_{\mathrm{in}}(1-\theta) = W_{\mathrm{out}}\theta. \qquad (13)$$

If λ is small compared to the reaction rate constant W_{rx}, then $B_{\mathrm{prod}} \to \lambda$. This means that almost every particle that enters the system is converted. If λ is much larger, then

$$B_{\mathrm{prod}} \to S\theta W_{\mathrm{rx}} \qquad (14)$$

for $\lambda/W_{\mathrm{rx}} \to \infty$ and S not too large. Figure 1 shows the θ dependence for small S and the S dependence for small θ. It does not show this S and θ dependence for S and θ both large, for which λ needs to be much larger than the values in the figure. For $S=100$ we see that the reactivity may be proportional to θ for $\theta \lesssim 0.5$, but not around $\theta=0.9$. For the latter value the reactivity is even smaller than for $\theta=0.5$.

In practice, only W_{in} can usually be varied independently. The limit $W_{\mathrm{in}} \to \infty$ corresponds to $\theta=1$ and $\lambda=W_{\mathrm{out}}$. So we see that there generally is an upper bound on λ.

Comparing $S=5$ and $S=100$ in Fig. 1 for some finite λ shows that B_{prod} varies less with θ for larger S. We can show that in the limit $S \to \infty$ the reactivity depends only on λ and W_{rx}. If the system becomes infinitely large, then the fluctuations become small with respect to the number of sites. If the system is then at steady state, we can write the master equation as

$$\frac{dP_N}{dt} = \lambda(P_{N+1}+P_{N-1}-2P_N). \qquad (15)$$

Formally we can let the number of particles N run from $-\infty$ to $+\infty$. The matrix $s-\mathbf{W}$ can easily be diagonalized.

The eigenvalues are $s+2\lambda(1-\cos k)$ with $-\pi<k\leq\pi$, and the corresponding eigenvector has components $\exp(ikN)$. We can use this to calculate elements of the inverse of the matrix $s-\mathbf{W}$:

$$[(s-\mathbf{W})^{-1}]_{NM}=\frac{1}{2\pi}\int_{-\pi}^{\pi}dk\frac{\cos(|N-M|k)}{s+2\lambda(1-\cos k)}$$

$$=\frac{1}{ys}\left[\frac{y-1}{y+1}\right]^{|N-M|} \qquad (16)$$

with

$$y=\sqrt{1+4\lambda/s}. \qquad (17)$$

This then yields for the probability that a particle enters and leaves at a later time without being converted the expression

$$\hat{f}_{N,N+1}(W_{\mathrm{rx}})=\frac{y-1}{y+1}. \qquad (18)$$

(Here and in the rest of the paper we set $s=W_{\mathrm{rx}}$ in the definition of y.) For the reactivity B_{prod} we have

$$B_{\mathrm{prod}}=\lambda[1-\hat{f}_{N,N+1}(W_{\mathrm{rx}})]=\tfrac{1}{2}W_{\mathrm{rx}}(y-1). \qquad (19)$$

We see that the reactivity no longer depends on the loading θ if the system becomes large, but only on the reaction rate and on λ. For small rates of particles entering and leaving we again find $B_{\mathrm{prod}}\to\lambda$. If the rates of entering and leaving are large, then

$$B_{\mathrm{prod}}\to(\lambda W_{\mathrm{rx}})^{1/2} \qquad (20)$$

for $\lambda/W_{\mathrm{rx}}\to\infty$. The approach to the limit $S\to\infty$ becomes very slow when λ is large as can be seen in Fig. 1.

The procedure for the first-passage problem above can also be used to derive the A and B profiles; i.e., the distribution of the A's and B's in the system. We will first deal with the question of what is the probability that the nth particle, counting from site 1, is an A. Then we will answer the question that site m is occupied by an A. The answers to the same questions about B's follow trivially from those of A's.

We are only interested in the steady state. In this case we have detailed balance; i.e., the number of transitions per unit time from N to $N+1$ particles is equal to those of $N+1$ to N. This means that for each sequence in the number of particles

$$N_0\overset{\to}{0}N_1\overset{\to}{\Delta t_1}N_2\overset{\to}{\Delta t_2}\cdots\overset{\Delta t_{T-1}}{\to}N_T=N_0, \qquad (21)$$

where after a time lapse Δt_i the number of particles changes from N_i to N_{i+1}, there is another sequence

$$N_0=N_T\overset{\to}{0}N_{T-1}\overset{\Delta t_{T-1}}{\to}N_{T-2}\overset{\Delta t_{T-2}}{\to}\cdots\overset{\to}{\Delta t_1}N_0. \qquad (22)$$

The second sequence is the time reversed sequence of the first one. Moreover, both sequences are equally likely because of the detailed balance. Consequently, the probability distribution that the number of particles in the system is K at time $t=0$ and M with $M<K$ at time $-t$ for the last time is

$f_{MK}(t)$. This means that if there are N particles in the system the probability distribution that particle n is in the system for a time t equals $f_{N-n,N}(t)$. The probability that that particle has not been converted is then $\hat{f}_{N-n,N}(W_{\mathrm{rx}})$ following the reasoning after Eq. (5). This probability can be calculated using Eq. (9).

For the profile we need the probability that site m is occupied by particle n. This probability is given by

$$P_{\mathrm{occ}}(n,N;m,S)=\binom{m-1}{n-1}\binom{S-m}{N-n}\Big/\binom{S}{N}. \qquad (23)$$

The probability $\langle A_m\rangle$ that site m is occupied by a particle that has not been converted is then given by

$$\langle A_m\rangle=\sum_{N=0}^{S}P_N^{(ss)}\binom{S}{N}^{-1}\sum_{n=1}^{m}\binom{m-1}{n-1}\binom{S-m}{N-n}\hat{f}_{N-n,N}(W_{\mathrm{rx}}), \qquad (24)$$

where the first summation averages over the number of particles in the system and $P_N^{(ss)}$ is given by Eq. (10).

The expression above can be simplified and interpreted more readily for an infinite system. With Eq. (16), we have

$$\hat{f}_{N-n,N}=\left(\frac{y-1}{y+1}\right)^n \qquad (25)$$

for the probability that particle n has not been converted. We see that this probability decreases exponentially.

The probability $P_{\mathrm{occ}}(n,N;m,S)$ becomes $P_{\mathrm{occ}}(n,m;\theta)$ with $\theta=N/S$ for $S\to\infty$. This limit of the combinatorial factors yields

$$P_{\mathrm{occ}}(n,m;\theta)=\binom{m-1}{n-1}\theta^n(1-\theta)^{m-n}. \qquad (26)$$

Substituting this expression and Eq. (25) in Eq. (24) yields

$$\langle A_m\rangle=\frac{\theta(y-1)(y+1-2\theta)^{m-1}}{(y+1)^m}. \qquad (27)$$

Again we find an exponential decrease but now with a characteristic length of $\Delta=1/[\ln(y+1)-\ln(y+1-2\theta)]$. For high loadings ($\theta\to1$) we find $\Delta\approx y/2$. For low loading ($\theta\to0$) we get $\Delta\approx(y+1)/(2\theta)$. So the characteristic length is larger for low loadings and higher rate of particles entering and leaving the system.

Figure 2 shows some typical profiles. The straight line corresponds to the exponential decrease of Eq. (27). The result for finite system sizes can be understood from the fact that smaller systems are less reactive because there are fewer sites at which conversion can take place. As the reactivity must be equal to the number of converted particles leaving the system, $W_{\mathrm{out}}\langle B_1\rangle$ must be smaller for smaller S, and because $\langle B_1\rangle=\theta-\langle A_1\rangle$ the curves in Fig. 2 must start out at larger values of $\langle A_1\rangle$. The reactivity also equals
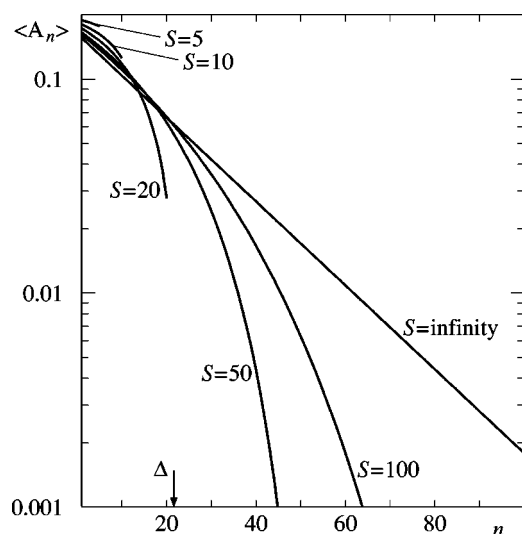
FIG. 2. The probabilities $\langle A_n \rangle$ that a site is occupied by an unconverted particle as a function of site index n for $\lambda = 16$, loading $\theta = 0.2$, and various system sizes S.

$W_{\mathrm{rx}} \Sigma_{n=1}^{S} \langle A_n \rangle$. This means that $\Sigma_{n=1}^{S} \langle A_n \rangle$ must be smaller for smaller S. Because $\langle A_1 \rangle$ is larger for smaller S, $\langle A_n \rangle$ must decrease faster.

Figure 2 confirms the slow convergence of the system to the limit $S \to \infty$. At $S = 100$ the values of $\langle A_n \rangle$ drop down to

2×10^{-5}. At such a low value, one would not expect an influence of these sites on the kinetics, but one clearly sees differences between $S = 100$ and $S \to \infty$ for all sites.

We would finally like to comment on three extensions of our model; particles entering and leaving at both ends, finite diffusion, and other reactions. A system with $2S$ sites and open at both ends has a reactivity that is twice that of a system with S sites and open at just one end provided that $S \gg \Delta$. DMC simulations show that if S is near or smaller than Δ, then the system open at both ends is relatively more reactive. (DMC simulations of our system open at one end yield, as they should, results identical to the analytical ones derived above.)

Finite diffusion is expected to be equivalent to infinite diffusion as long as it is much faster than other reactions. If this is not the case, then it may become a rate determining step. The system then becomes transport limited. As a consequence the reactivity can only go down. We have seen that in our simulations [10].

We expect that our results will change only little when we change the details of the reaction or when interactions between the particles are included [16]. Our results are a consequence of the nonpassing of the particles and of the fact that particles that stay longer in the system have a higher probability of being converted. We therefore also do not expect our results to change when we change our model of discrete sites to some continuous model.

[1] W.H. Meier, D.H. Olson, and C. Baerlocher, *Atlas of Zeolite Structure Types* (Elsevier, London, 1996).

[2] V. Privman, *Nonequilibrium Statistical Mechanics in One Dimension* (Cambridge University Press, Cambridge, 1997).

[3] H. van Beijeren, K.W. Kehr, and R. Kutner, Phys. Rev. B **28**, 5711 (1983).

[4] P.A. Fedders, Phys. Rev. B **17**, 40 (1978).

[5] K. Hahn and J. Kärger, J. Phys. Chem. **100**, 316 (1996).

[6] D. Keffer, A.V. McCormick, and H.T. Davis, Mol. Phys. **87**, 367 (1996).

[7] D. Schuring, A.P.J. Jansen, and R.A. van Santen, J. Phys. Chem. B **104**, 941 (2000).

[8] C. Rödenbeck, J. Kärger, and K. Hahn, J. Catal. **157**, 656 (1995).

[9] P.H. Nelson and S.M. Auerbach, J. Chem. Phys. **110**, 9235 (1999).

[10] S.V. Nedea, A.P.J. Jansen, J.J. Lukkien, and P.A.J. Hilbers, Phys. Rev. E **65**, 066701 (2002).

[11] R. Krishna, Chem. Phys. Lett. **326**, 477 (2000).

[12] J.G. Tsikoyiannis and J. Wei, Chem. Eng. Sci. **46**, 233 (1991).

[13] J. Kärger, M. Petzold, H. Pfeiffer, S. Ernst, and J. Weitkamp, J. Low Temp. Phys. **136**, 283 (1992).

[14] R.J. Gelten, R.A. van Santen, and A.P.J. Jansen, in *Molecular Dynamics: From Classical to Quantum Methods*, edited by P.B. Balbuena and J.M. Seminario (Elsevier, Amsterdam, 1999).

[15] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[16] D.S. Sholl and K.A. Fichthorn, Phys. Rev. Lett. **79**, 3569 (1997).