Exact 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 adsorption and desorption 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 adsorption and desorption. For large systems the number of nonconverted particles decreases exponentially with distance from the adsorption/desorption end.

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Zeolitic structures like mordenite, ZSM-22, and AlPO₄-5ₜ are industrially immensely important. They are examples of single-file systems (SFS). They have one-dimensional pores through which molecules can diffuse, but with cross sections that are too small to allow passing. As for many other 1D systems, this leads to very interesting kinetic effects. Research on SFS zeolites has focussed on the diffusion, because the mean-square displacement in a SFS is proportional to the square root of time, and not proportional to time. Molecular Dynamics, Dynamic Monte Carlo (DMC), and reaction-diffusion equations have mainly been used. Few studies have included reactions. 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 the pores.

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. In the current paper we derive exact results for the case that the entire pore is reactive. These results give detailed insight in 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 can be converted into a B on any site. Adsorption and desorption of particles can only occur on site 1. Only A’s are adsorbed, but both A’s and B’s desorb. Both types of particle diffuse by making random hops to neighboring sites if vacant.

The evolution of the system is described by a master equation

\[
\frac{dP_\alpha}{dt} = \sum_\beta [W_{\alpha\beta}P_\beta - W_{\beta\alpha}P_\alpha],
\]

(1)

where \(\alpha\) and \(\beta\) refer to the configuration of the adlayer (a particular distribution of particle over the sites), the \(P_\alpha\)’s are the probabilities of the configurations, \(t\) is real time, and the \(W_{\alpha\beta}\)’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 \(\beta\) into \(\alpha\). The rate constants in our model are \(W_{\text{ads}}\) for adsorption of an A onto site 1 if vacant, \(W_{\text{des}}\) for desorption of a particle from site 1, \(W_{\text{rx}}\) for the conversion of an A into a B on any site, and \(W_{\text{diff}}\) 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.

\[
\frac{dP_N}{dt} = W_{\text{ads}} \left[ 1 - \frac{N+1}{S} \right] P_{N-1} - W_{\text{ads}} \left[ 1 - \frac{N}{S} \right] P_N + W_{\text{des}} \frac{N+1}{S} P_{N+1} - W_{\text{des}} \frac{N}{S} P_N
\]

(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.

We are interested in the probability distribution \(f_{MN}(t)\) that if at time \(t = 0\) the number of particles is \(K\), this number becomes \(M\) for the first time at time \(t\) with \(M < K\). If there are \(N\) particles in the system and at time \(t = 0\) a particle adsorbs, then \(f_{N,N+1}\) is the probability distribution for the time that this particle desorbs. This is based on the property of a SFS that particles can not pass each other. So \(f_{N,N+1}\) is the probability distribution for the residence time of a particle that adsorbs in a system with \(N\) particles.

Let \(P_{NK}\) be the solution of Eq. (2) with \(N\) 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 adsorbing boundary at \(M\): i.e., we remove the term in Eq. (3) that corresponds to an adsorption then there are \(M\) particles in the system.

With \(N \geq M\) we have

\[
P_{NK}(t) = Q_{NK}(t) + \int_0^t dt' P_{NM}(t-t') f_{MK}(t').
\]

(3)
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

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

(4)

for $f_{MK}$.

A particle that adsorbs, stays in the system for a period $t$, and then desorbs, has a probability $\exp(-W_{rx} t)$ that it is not converted during the time it was in the system. Because the probability distribution for the time that it stayed in the system is given by $f_{N,N+1}(t)$, the probability that the particle desorbs without being converted is

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

(5)

This is equal to $\hat{f}_{N,N+1}(W_{rx})$ with $\hat{f}_{N,N+1}$ 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

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

(6)

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

$$\sum_M (s\delta_{NM} - W_{NM}) \hat{P}_M(s) = P_N(0)$$

(7)

With the initial condition for $P_{MK}$ this yields

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

(8)

so that

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

(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 the rate of adsorption and make a weighted average over the number of particles in the system. The probability that a particle is converted equals $1 - \hat{f}_{N,N+1}(W_{rx})$, and the rate of adsorption equals $W_{ads}(1 - S/N)$. At steady state the number of particles in the system is given by

$$P^{(ss)}_{N} = \left(\frac{S}{N}\right) \left[\frac{W_{ads}}{W_{ads} + W_{des}}\right]^S \left[\frac{W_{ads}}{W_{des}}\right]^N.$$  

(10)

Combining this results in

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

(11)

Figure 1 shows this reactivity for two finite system sizes and three loadings. The loading $\theta$ is defined as the probability that a site is occupied at steady state. It’s equal to

$$\theta = \frac{W_{ads}}{W_{ads} + W_{des}}.$$  

(12)

The reactivity is compared to the (average) rate of adsorption and desorption $\lambda$, which at steady state is given by

$$\lambda = W_{ads}(1 - \theta) = W_{des}\theta.$$  

(13)

If the rates of adsorption and desorption are small compared to the reaction rate constant $W_{rx}$, then $B_{prod} \rightarrow \lambda$. This means that almost every particle that enters the system is converted. If the rates of adsorption and desorption are much larger, then

$$B_{prod} \rightarrow S\theta W_{rx}.$$  

(14)

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

In practice only $W_{ads}$ can usually be varied independently, either through the pressure or the concentration of A’s outside the system. The limit $W_{ads} \rightarrow \infty$ corresponds to $\theta = 1$ and $\lambda = W_{des}$. So we see that there generally is an upper bound on $\lambda$. 

![Figure 1](image-url)
Comparing $S = 5$ and $S = 100$ in Fig. [3] for some finite
\( \lambda \) shows that $B_{\text{prod}}$ varies less with $\theta$ for larger $S$. We
can show that in the limit $S \to \infty$ the reactivity depends
only on $\lambda$ and $W_{\text{rx}}$. 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
\[
\frac{dP_N}{dt} = \lambda(P_{N+1} + P_{N-1} - 2P_N).
\]
(15)

Formally we can let the number of particles $N$ run from
$-\infty$ to $+\infty$. The matrix $s - W$ can easily be diag-
onalized. The eigenvalues are $s + 2\lambda(1 - \cos k)$ with
$-\pi < k \leq \pi$, and the corresponding eigenvector has com-
ponents $\exp[ikN]$. We can use this to calculate elements
of the inverse of the matrix $s - W$.
\[
[(s - W)^{-1}]_{NM} = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{\cos((N - M)k)}{s + 2\lambda(1 - \cos k)} \, dk
= \frac{1}{ys} \begin{bmatrix} y - 1 \\ y + 1 \end{bmatrix}^{y - 1 - N - M}.
\]
(16)

with
\[
y = \sqrt{1 + 4\lambda/s}.
\]
(17)

This then yields for the probability that a particle ad-
sorbs and desorbs at a later time without being converted
the expression
\[
\hat{f}_{N,N+1}(W_{\text{rx}}) = \frac{y - 1}{y + 1}.
\]
(18)

(Here and in the rest of the paper we set $s = W_{\text{rx}}$ in
the definition of $y$.) For the reactivity $B_{\text{prod}}$ we have
\[
B_{\text{prod}} = \lambda[1 - \hat{f}_{N,N+1}(W_{\text{rx}})] = \frac{1}{2} W_{\text{rx}}(y - 1).
\]
(19)

We see that the reactivity no longer depends on the load-
ing $\theta$ if the system becomes large, but only on the reaction
rate and on $\lambda$. For small rates of adsorption and desor-
ation we again find $B_{\text{prod}} \to \lambda$. If the rates of adsorption
and desorption are large, then
\[
B_{\text{prod}} \to (\lambda W_{\text{rx}})^{1/2}
\]
(20)

for $\lambda/W_{\text{rx}} \to \infty$. The approach to the limit $S \to \infty$
becomes very slow when $\lambda$ is large as can be seen in
Fig. [3].

The procedure for the first-passage problem above can also be
used to derive the A and B profiles: i.e., the distribu-
tion of the A’s and B’s in the chain. We will first deal
with the question what the probability is that the
$n$th 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 the ones for the 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

\[
N_0 \rightarrow N_1 \rightarrow N_2 \rightarrow \ldots \rightarrow N_T = N_0,
\]
(21)

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

\[
N_0 = N_T \rightarrow N_{T-1} \rightarrow N_{T-2} \rightarrow \ldots \rightarrow N_1 \rightarrow N_0.
\]
(22)

The second sequence is the time reversed of the first one.
Moreover, both sequences are equally likely because of the
detailed balance. Consequently, the probability distri-
bution that the number of particles in the system is
\( N \) at time $t = 0$ and $M$ with $M < K$ at time $-t$ for the
last time equals $f_{MK}(t)$. 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 $f_{N-n,N}(W_{\text{rx}})$ following the rea-
soning after Eq. (5). This probability can be calculated
using Eq. (16).

For the profile we need the probability that site $m$ is
occupied by particle $n$. This probability is given by
\[
P_{\text{occ}}(n, N; m, S) = \binom{m - 1}{n - 1} \frac{S - m}{N - n} / \binom{S}{N}.
\]
(23)

The probability $\langle A_m \rangle$ that site $m$ is occupied by a particle
that has not been converted is then given by
\[
\langle A_m \rangle = \sum_{N=0}^{S} P_N^{(ss)} \binom{S}{N}^{-1}
\times \sum_{n=1}^{m} \binom{m - 1}{n - 1} \frac{S - m}{N - n} \hat{f}_{N-n,N}(W_{\text{rx}})
\]
(24)

where the first summation averages over the number of
particles in the system and $P_N^{(ss)}$ is given by Eq. (16).

The expression above can be simplified and interpreted
more readily for an infinite system. With Eq. (16) we have
\[
\hat{f}_{N-n,N} = \left(\frac{y - 1}{y + 1}\right)^n
\]
(25)

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

The probability $P_{\text{occ}}(n, N; m, S)$ becomes $P_{\text{occ}}(n, m; \theta)$
with $\theta = N/S$ for $S \to \infty$. This limit of the combinatorial
factors yields
\[
P_{\text{occ}}(n, m; \theta) = \binom{m - 1}{n - 1} \theta^n (1 - \theta)^{m-n}.
\]
(26)
substituting this expression and (23) in (24) yields
\[
\langle A_n \rangle = \frac{\theta(x-s)(x+s-2\theta s)^{m-1}}{(x+s)^m}.
\] (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 (\( \theta \rightarrow 1 \)) we find \( \Delta \approx y/2 \). For low loadings (\( \theta \rightarrow 0 \)) we get \( \Delta \approx (y + 1)/(2\theta) \). So the characteristic length is larger for low loadings and higher rate of adsorption and desorption.

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 desorbing converted particles, \( W_{des}(B_1) \) 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 \( W_{rx} \sum_{n=1}^{S} \langle A_n \rangle \). this means that \( \sum_{n=1}^{S} \langle A_n \rangle \) 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 \( S \rightarrow \infty \). at \( S = 100 \) the values of \( \langle A_n \rangle \) drop down to \( 2 \times 10^{-5} \). at such low value one would not expect an influence of these sites on the kinetics, but one clearly sees differences between \( S = 100 \) and \( S \rightarrow \infty \) for all sites.

we would finally like to comment on three extensions of our model: adsorption and desorption at both ends, finite diffusion, and other reactions. a system with 25 sites and adsorption and desorption at both ends has a reactivity that is twice the one of a system with \( S \) sites and adsorption and desorption at just one end provided that \( S \gg \Delta \). dmc simulation show that if \( S \) is near or smaller than \( \Delta \), then the system open at both ends is relatively more reactive.

finite diffusion is expected to be equivalent to infinite diffusion as long as it is much faster than the 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. we expect that our results will change only little when we change the details of the reaction or when interaction between the particles are included. our results are a consequence of the non-passing 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.

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