Reaction order versus reaction probability for bimolecular steady state reactions: A+A→A and A+A→0 in one dimension

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Reactions of A+A→product on one-dimensional lattices with steady state input sources are simulated with various local reaction probabilities, P. Among others the reaction order, X, is examined at different P. Our results demonstrate that X goes down from 3 to 2 as P goes from 1 to 0. The nearest neighbor distance distribution (NNDD) for the reaction A+A→0 at $P=1.0$, i.e. diffusion-limited reaction, follows the previously reported skewed exponential shape. This is no longer true for $P < 1$. Similarly, for the reaction A+A→A, the NNDD changes with P. Finally, at $P \to 0$, as expected, an exponential (Poissonian) distribution is obtained for both reactions.

1. Introduction

The textbook rate equation for the elementary reaction A+A→products, with transient batch condition, is usually written as

$$\frac{d\rho}{dt} = -k\rho^2 , \qquad (1)$$

where ρ is the density of the reactant and k is the reaction coefficient. On one hand, the product can be a species that whenever formed will leave the system immediately or one that is inert so that it does not participate in any further reactions. This type of reaction can be formulated by A+A→0 ("annihilation"). On the other hand, if the reaction is a "fusion" type reaction, the product may be exactly the same species as the reactant except that one of them disappears after the reaction. While strict "fusion" reactions may only occur in exotic situations such as exciton fusion (see below), already Smoluchowski has treated coagulation reactions with this model [1] and it is still used for dimerization and polymerization reactions [2].

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Occasionally the real reaction is bounded by the "annihilation" and the "fusion" case:

$$A+A\to 0 ,$$
$$A+A\to A . \qquad (2)$$

This is the situation for triplet-exciton–triplet-exciton fusion (annihilation) [3], where the fusion is much more likely than the annihilation process. Recently, similar exciton reactions were performed by us on isolated polymer chains, with a strictly one-dimensional topology [4,5]. This stimulated the present work.

It has been demonstrated over the last decade that when a diffusion-limited elementary bimolecular reaction is carried out in media less than three dimensional, the reaction order may not be an integer any more and it may well be above the commonly accepted value of two [6–11]. Specifically, in the presence of a steady state source of reactant A, with the adding rate R, eq. (1) is replaced by

$$\frac{d\rho}{dt} = R - k\rho^X , \qquad (3)$$

where X is the reaction order, which is 2 for classical reaction kinetics. Recent computer simulations [12],

theoretical work [13] and experiments [5,14] have demonstrated that X can be a number bigger than 2 for reactions carried out in media with dimensionality smaller than 3 or on fractal spaces. For both the $A+A\rightarrow A$ and $A+A\rightarrow 0$ reactions in 1-D media and within the diffusion-limited regime, there is now agreement that the reaction order $X\rightarrow 3$. For a reaction-limited reaction, however, we believe that $X=2$ still holds, and is independent of the reaction medium. This question is addressed below.

In this paper we report the relation of the steady-state reaction order X with the local reaction probability, P, for the reactions $A+A\rightarrow 0$ and $A+A\rightarrow A$ on 1-D lattices. When $P=1.0$, the reaction is a diffusion-limited one, while when $P\rightarrow 0$, it is considered to be a reaction-limited reaction. Indeed, for $P=1.0$ we confirm the non-classical result for the low-dimensional reaction media. On the other hand, for $P\rightarrow 0$, the classical result is confirmed. However, for P ranging between 0 and 1.0, the X values have not been determined before. Our simulations appear to give the first information on the behavior of X with P. We note here that for one-dimensional *batch* reactions [15], the asymptotic ($t\rightarrow\infty$) results are $X=3$ for all P (except that $X=2$ for $P\rightarrow 0$). However, this is not the case found here for the *steady state* reactions. Also the interparticle distribution functions are found to change with P.

2. Methods of simulations

In all these simulations, a 1-D lattice with 50000 sites is used. Preset adding rates, such as 1, 2 or 10 walkers per time step, are used to randomly add the required number of walkers to the system at each time step. If the chosen site has been occupied already then another site is chosen randomly. At each step this process is repeated until all the added walkers find their positions on the lattice. Once the landing process is over all the present walkers in the system are moved once. With cyclic boundary conditions, each walker has equal possibility to move to the left and to the right of its present position.

The motion of the walkers always starts with walker no. 1 although walker no. 1 may not be the same one at each step due to reactions. All the walkers in the system have infinite lifetimes. That is, once landed

in the lattice they will remain in the system unless they are eliminated by reactions. If at a given time step, two reactants happen to occupy the same lattice site, there is a tendency for the reaction to occur. This depends on the preset reaction probability, P (P is set at the beginning of the simulation). If P equals 1 (the diffusion limited reaction), a product will be formed whenever two reactants collide. If P is less than one, then when two reactant collide, a random number is picked and compared to the P value and the "reaction or no reaction" decision is made. If the reaction is not to occur, the two reactants will remain in their locations and the presently moving reactant is not considered any more during this time step. For the reaction $A+A\rightarrow 0$ the product of a successful reaction will leave the system. However, for the reaction $A+A\rightarrow A$ a successful reaction means that the moving particle is removed from the system, while the one it collides with survives. At each time step, the number of remaining walkers in the system is recorded. After all the walkers in the system have been moved once the first time step is over and the "clock" is incremented by one and the system is ready for another landing of walkers.

When the density of the reactant does not change with time, that is when $\rho(t)=$ const., the system can be said to be in its *steady state*. In practice, the density does fluctuate even when the system is considered to be at its steady state. In order to ensure that this fluctuation does not affect the simulation results, the time window over which the average number of walkers is calculated is usually long enough so that the average is the true representative of the system. In our simulations the typical length of the time window used to calculate the average number of particles, N_{ss}, is 25000 steps. The systems are well in the steady state after the first 25000 steps. Therefore a total of 50000 steps are used in all the simulations except that for $P=0.001$ and 2 walkers per 10 steps (0.2 walker per each step) 200000 total steps were used to ensure that the system has reached steady state.

When two adjacent reactants collide and the reaction does not occur these two walkers will remain one lattice apart neighbors. The nearest neighbor distance distribution (NNDD), which is essentially the same as the gap distribution [16,17], is obtained by calculating the distance of each walker from its near-

est neighbors. In our program this is done by first finding the ith walker's coordinate, x_i ($i=1, 2, ..., N$, where N is the total number of walkers in the system). Then the searching for the nearest neighbor starts with lattice sites $x_i \pm 1$. If a walker is found then the nearest neighbor distance is 1, otherwise the coordinates are incremented by 1 in both right and left directions, i.e. $x_i \pm 2$. This process is continued until one or two reactants are encountered. When the nearest neighbor is found, no matter one or two, the distance only contributes once to the whole distribution spectrum. In other words, for any given walker only one nearest neighbor distance is recorded. One should note that if the ith walker's nearest neighbor is the jth walker, this does not guarantee that the jth walkers's nearest neighbor is the ith walker unless they are only one lattice apart.

3. Results and discussion

It is easy to understand that at a fixed reaction probability, P, the more particles added at each step, the faster the steady state is reached (see fig. 1, for example. Only the $A+A \rightarrow 0$ result is given here). This is simply because when more particles are present in the system they have a better chance to encounter each other and react. This is also the reason that at a fixed landing rate, say 2 walkers per step, the bigger P, the less time it takes for the steady state to occur. This result can be seen from fig. 2. For the same reason, the more reactants are consumed, the quicker the steady state can be reached. The system of $A+A \rightarrow 0$

Fig. 2. Normalized walker population versus time steps (100 runs) for the reaction $A+A \rightarrow 0$ with 2 walkers per step at $P=0.001$, 0.01, 0.1 and 1.0 (from right to left).

Fig. 3. Normalized walker population versus time steps (100 runs) for reactions $A+A \rightarrow 0$ and $A+A \rightarrow A$ with 2 walkers per step at $P=0.01$.

is thus expected to reach steady state faster than that of $A+A \rightarrow A$, when the same P and the same landing rate are used. One also expects a smaller steady state walker density for the reaction $A+A \rightarrow 0$ than that for $A+A \rightarrow A$, based on the above arguments. The simulation results, which are presented in figs. 3 and 4,
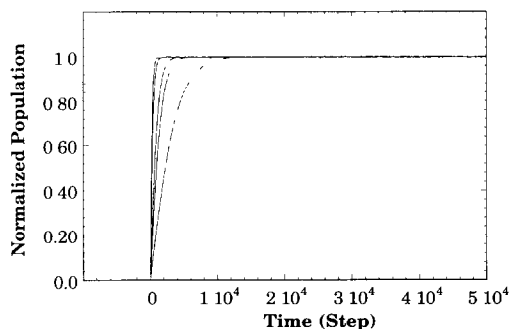

Fig. 1. Normalized walker population versus time steps (100 runs) for the reaction $A+A \rightarrow 0$ at $P=0.01$ with 0.2, 1, 2, 10 and 20 walker(s) per step (from right to left).
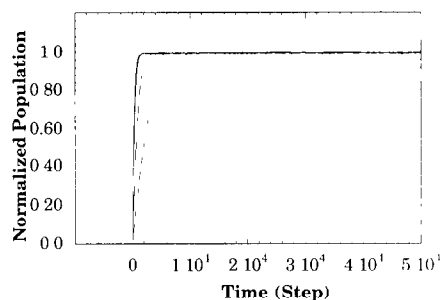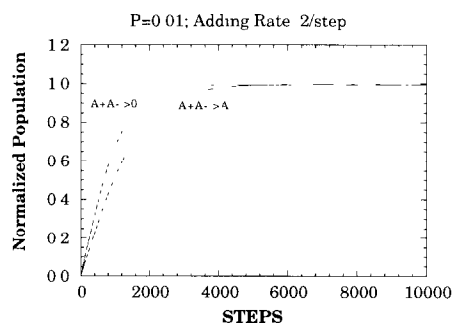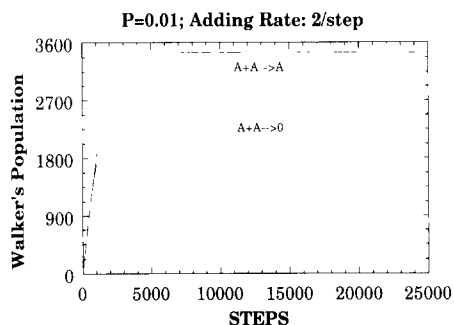

Fig. 4. Walker population versus time steps for reactions $A+A \rightarrow 0$ and $A+A \rightarrow A$ with 2 walkers per step at $P=0.01$ (average from 100 runs).

agree well with the above expectations.

At steady state, $dp/dt=0$, and therefore eq. (3) can be simplified as

$$R=kp^X.\tag{4}$$

Eq. (4) can also be written as

$$\frac{J}{L}=k\left(\frac{N_{ss}}{L}\right)^X,\tag{5}$$

where J is the number of walkers added per time step, L is the number of lattice sites and N_{ss} the average number of walkers at steady state. By taking the logarithm of both sides of eq. (5) and a linear square fit of $\log(J)$ versus $\log(N_{ss})$, the slope of the plot, which is X, can easily be obtained. Also, from the intercept of the above log–log plot the reaction coefficient k can be calculated.

In figs. 5a and 5b we plot $\log(N_{ss})$ versus $\log(J)$ for $P=0.001, 0.01, 0.1$ and 1.0, respectively, for both reactions. For each P value we use five different landing rates whic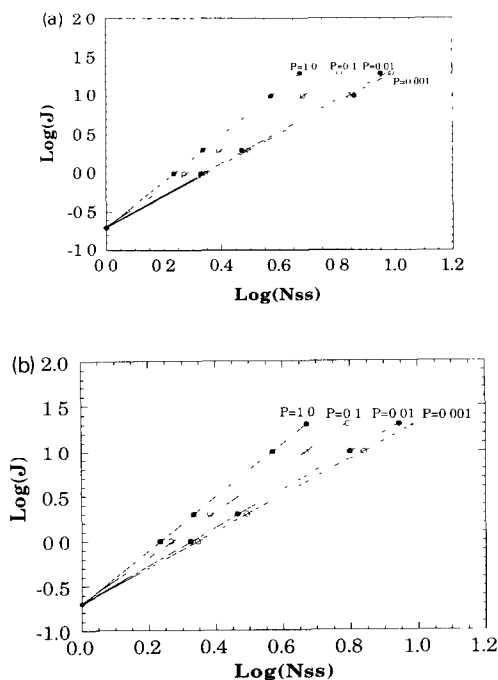h cover two orders of magnitude. An important result is the constancy of the order X over the investigated density range (note the linear fits). The value of N_{ss} is normalized to that of 2 walkers per 10 steps. This normalization does not affect the slopes of the plots, i.e. X (but it does affect the intercept). From this figure one sees that for both reactions the reaction order at $P=0.01$ is closer to that at $P=0.001$ than to that at $P=0.1$. In other words, the reaction order X has a sharp change in the region of around 0.1. This can be clearly seen from fig. 6, where X is plotted versus P. When $P=0.001$, X is close to 2, i.e. to that of reaction-limited kinetics. However, for $P=1.0$ a reaction order close to 3 is obtained indicating a non-classical, diffusion-limited reaction regime. At a specific reaction probability, P, the X value for the reaction $A+A\rightarrow A$ is always slightly higher than that for $A+A\rightarrow 0$. This may indicate that for the same P, the reaction $A+A\rightarrow A$ slightly favors diffusion-limited kinetics compared to that of $A+A\rightarrow 0$.

In table 1 we list the reaction rate coefficients for the reaction $A+A\rightarrow 0$ with $P=0.001, 0.01, 0.1$ and 1.0, respectively. They generally follow the trend that the higher the reaction probability, the larger the reaction coefficient (note, however, that their units also change with P, i.e. with X). In table 2 are given the

Fig. 5. Log(N_{ss}) versus log(J) for (a) the reaction $A+A\rightarrow 0$ and (b) the reaction $A+A\rightarrow A$ when different P_s are used. Note that for each P, the N_{ss} is normalized to that with 0.2 walker per step. The slopes give the X values (results from 100 runs).
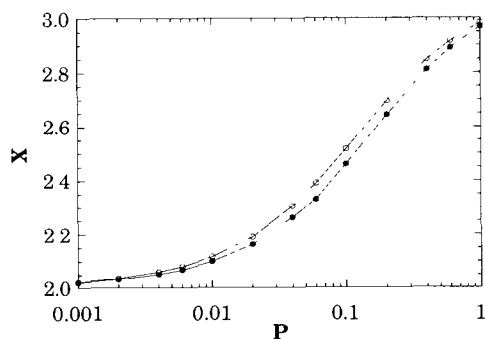

Fig. 6. Reaction order X versus reaction probability P for reactions $A+A\rightarrow 0$ (●) and $A+A\rightarrow A$ (○).

Table 1
Reaction coefficients k versus reaction probability P (100 runs)

P	k
0.001	0.0020
0.01	0.0231
0.1	0.513
1.0	2.748

Table 2
Density ρ at steady state with different adding rates (100 runs)

R	P			
	0.001	0.01	0.1	1.0
2/10 steps	0.0458	0.0163	0.00855	0.00734
1/step	0.101	0.0346	0.0160	0.0126
2/step	0.143	0.0481	0.211	0.0159
10/step	0.317	0.104	0.0412	0.0274
20/step	0.447	0.145	0.0554	0.0346

reactant densities at steady state with the above four P values. They agree with the trend that the higher the P, the bigger the k and the smaller the reactant density. However, the effect of the higher X is also evident in the less sharp rise of the steady state density with R at high P. We note that in classical kinetics $k \sim P$ (for constant reaction order X). This obviously is not the case here (even the units of k change with P). Similar overall trends are obtained for the reaction $A+A \rightarrow A$, which are not listed here, although the density at any given P and landing rate is larger than that of the corresponding reaction $A+A \rightarrow 0$.

If the reaction probability is very very small the reactants will get close to a random (Poissonian) distribution. This will result in changes in the NNDD. Again one can see that when P increases from 0.001 to 1.0 the shapes of the NNDD curves undergo a sharp change. With $P=1.0$ one expects a skewed exponential distribution of the nearest neighbors for reaction $A+A \rightarrow 0$ [17,18] and an Airy function shape [16] for reaction $A+A \rightarrow A$. At steady state with decreasing P the NNDD approaches a Poissonian (simple exponential) shape for both reactions when $P \rightarrow 0$. These results can be seen from figs. 7a and 7b. Here $\langle r \rangle$ is the average distance between reactants in the lattice at steady state, which is the reciprocal of the reactant density. At $P=0.001$, for both reactions there are relatively large discrepancies between the simulated data and the exponential fitting curves at small $\langle r \rangle$. This deviation may be explained by the fact that the exponential curve for the NNDD is the result of $P \rightarrow 0$, i.e. there is no reaction at all. With reaction probability $P=0.001$, however, the reaction is still not totally in the reaction-limited regime!
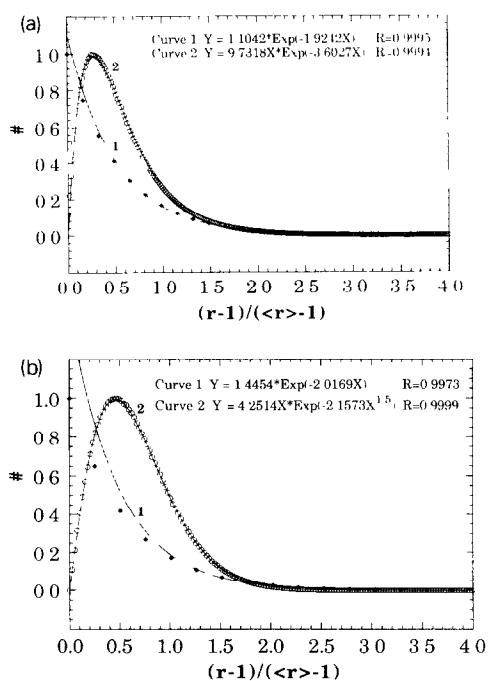
Figs. 8a and 8b illustrate the NNDD curves versus

Fig. 7. NNDD versus $(r-1)/(\langle r \rangle -1)$ for (a) reaction $A+A \rightarrow 0$ and (b) reaction $A+A \rightarrow A$ with 2 walkers per step adding rate at $P=0.001$ and 1.0 (results from 100 runs). The solid lines are the fitted curves. Curve 1: exponential ($P=0.001$); curve 2: skewed exponential ($P=1.0$) for reaction $A+A \rightarrow 0$. Note that for $A+A \rightarrow A$ a different fitting curve than that of $A+A \rightarrow 0$ at $P=1.0$ is used (see text).

different P at a fixed landing rate of two walkers per step. These results show that the NNDD curves for $P=0.01$ are more similar to that for $P=0.001$ than to that for $P=0.1$, while for $P=0.1$ the curve is closer to that of $P=1.0$. These results agree well with those in fig. 5.
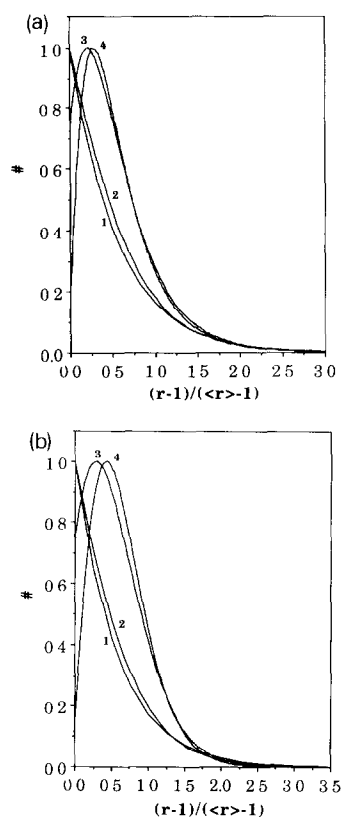
At a specific P, the shapes of the NNDD curves are

Fig. 8. NNDD versus $(r-1)/(\langle r \rangle-1)$ for (a) reaction $A+A\to 0$ and (b) reaction $A+A\to A$, with four different reaction probabilities. Adding rate is 2 per step for all four of them. From curve 1 to 4, $P=0.001, 0.01, 0.1$ and 1.0, respectively (rsults from 5000 runs).

Fig. 9. (a) NNDD versus $(r-1)/(\langle r \rangle-1)$ for reaction $A+A\to 0$ with $P=0.01$ with 0.2, 2 and 20 walker(s) per step, respectively. (b) Same as (a) except that NNDD is plotted against r. The symbols are the simulated data and the solid lines the exponential fitting curves (results from 5000 runs).

not affected by the number of particles added at each step. One should note that this is true only if the NNDD curves are plotted in a normalized form as done here. If one plots the NNDD with r instead of $(r-1)/(\langle r \rangle-1)$, the more walkers added at each step the faster decay the NNDD curves will show. However, the basic form of the function will not change. These results can be seen from figs. 9a and 9b.

It may appear that having a finite reaction probability $0<P<1$ is equivalent to having a reverse reaction, e.g. the dissociation $A\to A+A$. However, for the reversible reactions that are usually treated in the literature [2], the assumption is that there is no steady state source, only an internal one (the dissociation). Under these circumstances it is obvious that the
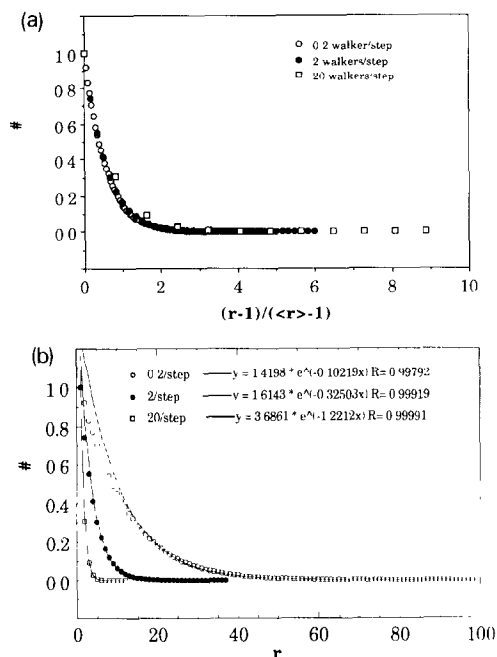
steady state of the reversible reaction is an equilibrium state. For equilibrium reactions the classical answer is always valid. Likewise, the particle distribution (NNDD) is always Poissonian (i.e. random). The latter is the embodiment of the Maxwell postulate (random distribution at equilibrium) which underlies the classical reaction laws [6].

4. Conclusions

With changes in reaction probability, we observe sharp changes of the reaction orders, X, with P, at around $P=0.1$ for both the $A+A\to A$ and $A+A\to 0$ reactions on a 1-D lattice. At the two extreme values of P, the reaction- and diffusion-limited kinetics are verified, giving $X=2$ and 3, respectively. Both the reaction rate coefficient and the reactant density follow this trend. The NNDD for the $A+A\to 0$ reaction changes from skewed exponential shape to one which is close to exponential (Poissonian) when $P\to 0$.

Similarly, for the reaction $A + A \rightarrow A$ the NNDD is an Airy function at $P = 1.0$ and changes continuously towards an exponential form at $P \rightarrow 0$.

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