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Three-state model for cooperative desorption on a one-dimensional lattice

F. Vikas, F. Baras, and G. Nicolis
Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles, Campus Plaine, Caixa Postal 231,
B-1050 Brussels, Belgium

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We develop a master equation approach to the dynamics of immobile reactants on a one-dimensional lattice, in the presence of two different species undergoing cooperative desorption. A common feature of all the schemes studied is the strong dependence of the final coverage on the initial conditions, associated with the lack of ergodicity of the invariant state. Our approach leads to full agreement with Monte Carlo simulations, both asymptotically and transiently.

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I. INTRODUCTION

Recently, there has been a great deal of interest in phenomena that take place on sets of low dimensionality. Very diverse systems, such as interacting spins, random walks, percolation clusters, reactive schemes, and so on, turn out to present here a radically different macroscopic behavior than the one predicted by the mean-field (MF) approach. The origin of the deviations has been successfully identified and appears to depend on both the characteristics of the support and the nature of the underlying dynamics [1–5].

Most of the literature on the effects of dimensionality on the dynamical behavior of reactive systems focuses on diffusion-controlled reactions. As the spatial dimension decreases, so does the reactants' mobility, resulting in less efficient transport and a slowing down of the reaction. This effect can be enhanced if the support is of discrete nature, the relevant parameter being then the coordination number of the lattice, rather than its dimension.

In a series of papers [6–10], the present authors have considered the opposite limit where the reactants remain immobile within the time scale of interest, thereby focusing on the reaction dynamics and its role in the global behavior for various types of kinetics. In all the cases studied the embedding in a lattice, with hard core exclusion and short range reactive interactions, causes a quantitative or qualitative change from MF behavior. In particular, in the dynamics of irreversible reactions on a one-dimensional lattice, $A+A\rightarrow A+S$ and $A+A\rightarrow S+S$, referred to cooperative partial and full desorption (or, more popularly, coagulation and annihilation) [10], some particles are left on the lattice indefinitely, resulting in a nonzero coverage of the lattice in the asymptotic time limit, whereas the MF equations predict a hyperbolic decrease of the coverage. The time evolution equations for clusters of particles has been derived from a Glauber-type master equation [11], and their solutions lead to analytic expressions for the lattice occupation that are in full agreement with the results of numerical simulations. Note that the second reaction, whose solution was originally given by Flory [12], is equivalent to a random sequential adsorption process (RSA). These systems have since then been given considerable attention, as can be seen in Ref. [13].

In the present paper, we take the problem one step further by considering reactive schemes involving two different species. A site can now be found in three different states, the third one being the state of vacancy. Such problems have attracted attention in the recent literature [14–16], the usual approach being to map them to a quantum mechanical formalism. Here we develop an alternative approach based on a Glauber-type master equation.

The particular systems analyzed here are still associated with cooperative desorption, in two different ways.

Scheme (1a):

$$A+A\xrightarrow{\ell_1}A+P,\quad P\xrightarrow{k_2}S. \tag{1a}$$

Scheme (1b):

$$A+A\xrightarrow{\ell_1}P+P,\quad P\xrightarrow{k_2}S. \tag{1b}$$

We refer to these schemes as stepped desorption. They are an extension of those studied previously [10]. The difference is that, here the reaction between *A* particles produces a product *P* that desorbs spontaneously, leaving an empty site *S*.

Scheme (2):

$$A+B\xrightarrow{k_1}S+S. \tag{2}$$

This two-species desorption is known to present very interesting features when diffusion is allowed. After some time, reactant segregation occurs, slowing down the reaction that only takes place at the interfaces. The present work will shed further light on these phenomena.

In Sec. II, we describe the MF behavior for the various schemes, which turns out to be nontrivial for the stepped desorption case. Section III is devoted to the derivation of an extended Glauber type master equation. This equation is used in Secs. IV and V, where a solution for the coverage of the lattice in the case of, respectively, stepped desorption and two-species desorption is computed and found to be in full agreement with numerical simulations, both asymptotically and transiently. Finally, our conclusions are summarized in Sec. VI.

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II. MEAN-FIELD DESCRIPTION

In this section we summarize the mean-field results for the two models introduced above. We first consider scheme (1a). With a proper dimensionalization, steps (1a) are described by the following rate equations:

$$\frac{da(\tau)}{d\tau}=-a(\tau)^2,\qquad \epsilon\frac{dp(\tau)}{d\tau}=\epsilon a(\tau)^2-p(\tau),$$

$$\epsilon\frac{ds(\tau)}{d\tau}=p(\tau),$$

where $\tau=k_1 t$, $\epsilon=k_1/k_2$, and $k_1=\ell_1 A(0)$. The exact solution can be put in the form

$$a(\tau)=\frac{1}{\tau+\dfrac{1}{a(0)}},$$

$$p(\tau)=[a(0)+p(0)]e^{-\tau/\epsilon}-\frac{1}{\tau+\dfrac{1}{a(0)}}+\frac{1}{\epsilon}e^{-(1/\epsilon)\{\tau+[1/a(0)]\}}\left\{E_i\left[\frac{1}{\epsilon}\left(\tau+\frac{1}{a(0)}\right)\right]-E_i\left(\frac{1}{\epsilon a(0)}\right)\right\},$$

$$s(\tau)=s(0)+\frac{1}{\epsilon}\int_0^\tau p(\tau')d\tau'.$$

As we can see, it involves the exponential integral function that does not have an approximate analytical form in the positive domain. To compute a solution for $s(\tau)$ in a more explicit form, we consider the case $\epsilon\ll 1$, or in other words, a desorption reaction much faster than the alteration reaction, and apply singular perturbation theory.

The starting point is to seek for a solution in the form of a power series of ϵ,

$$p(\tau)=\sum_{r=0}^{\infty}p_r(\tau)\epsilon^r. \tag{3}$$

Tihonov's theorem asserts that such a solution exists. Then it appears that the actual solution is a linear combination of three such series that will always be a uniform approximation of the true solution inside and outside the system's boundary layer. More details can be found in Secs. 39 and 40 of Ref. [17]. Keeping terms up to order ϵ^2, one finds

$$a(\tau)=\frac{1}{\tau+\dfrac{1}{a(0)}},$$

$$p(\tau)=p(0)e^{-\tau/\epsilon}+\epsilon\left[\frac{1}{\left(\tau+\dfrac{1}{a(0)}\right)^2}-a(0)^2e^{-\tau/\epsilon}\right]+\epsilon^2\left[\frac{2}{\left(\tau+\dfrac{1}{a(0)}\right)^3}-2a(0)^3e^{-\tau/\epsilon}\right]+O(\epsilon^3), \tag{4}$$

$$s(\tau)=s(0)+p(0)(e^{-\tau/\epsilon}-1)+\epsilon\left[a(0)^2e^{-\tau/\epsilon}-\frac{1}{\left(\tau+\dfrac{1}{a(0)}\right)^2}\right]+O(\epsilon^2).$$

Note that the solution for $s(\tau)$ is directly integrated from $p(\tau)$ equation, which explains its lower order of approximation. A similar derivation for scheme (1b) leads to the approximate solution of order ϵ^2,

$$a(\tau)=\frac{1}{2\tau+\dfrac{1}{a(0)}},$$

$$p(\tau)=p(0)e^{-\tau/\epsilon}+2\epsilon\left[\frac{1}{\left(2\tau+\dfrac{1}{a(0)}\right)^2}-a(0)^2e^{-\tau/\epsilon}\right]+2\epsilon^2\left[\frac{1}{\left(2\tau+\dfrac{1}{a(0)}\right)^3}-a(0)^3e^{-\tau/\epsilon}\right]+O(\epsilon^3), \tag{5}$$

$$s(\tau)=s(0)+p(0)(e^{-\tau/\epsilon}-1)+2\epsilon\left[a(0)^2e^{-\tau/\epsilon}-\frac{1}{\left(2\tau+\dfrac{1}{a(0)}\right)^2}\right]+O(\epsilon^2).$$

Figure 1 shows the convergence of these solutions towards the exact one, for both the schemes.

For scheme (2), we do not meet such difficulties and the solution is found to decrease as t^{-1}.

III. MASTER EQUATION FOR A THREE-STATE MODEL

In this section we derive a master equation for a general system where the processes involved affect at most two sites. For the sake of simplicity, mainly to prevent any overcounting, we assume that a two-site event can happen only between a site i and its right-hand neighbor $i+1$. Since we work on a ring, this does not entail any loss of generality. This kind of formalism was used previously for two-state problems and proved to be suitable for the study of such systems [10]. Its generalization to three-state models proceeds as follows.

We consider a set of L spinlike variables $\sigma=\pm 1,0$ ar-

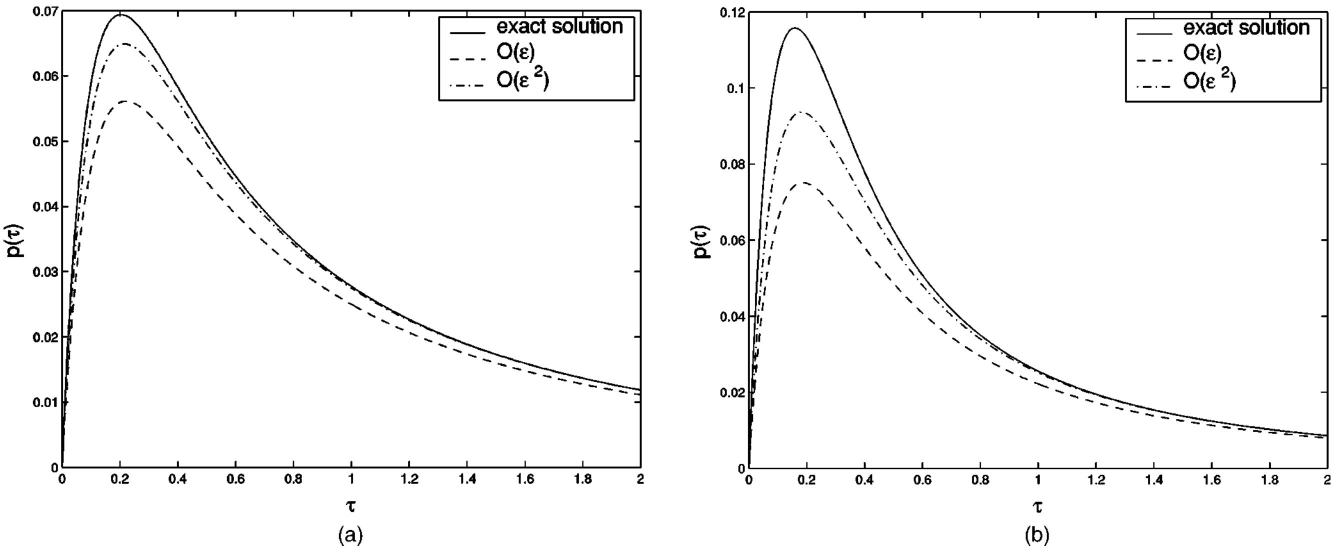


FIG. 1. MF behavior for $p(\tau)$ for the (a) partial and (b) full stepped desorption, with initial conditions $a(0)=1$, $p(0)=0$, $s(0)=0$, for $\epsilon=0.1$. The approximate solutions of orders ϵ and ϵ^2 clearly converge in both the schemes towards the exact solution.

ranged on the sites j of a one-dimensional ring. Starting from some arbitrary initial state, the evolution in time of the probability distribution $P(\{\sigma^1\};t)$ is described by the master equation

$$\frac{dP(\{\sigma^1\};t)}{dt}=-\sum_j\sum_{q=2}^{7} w_j(\{\sigma^1\}\to\{\sigma^q\},t)P(\{\sigma^1\};t)+\sum_j\sum_{q=2}^{7} w_j(\{\sigma^q\}\to\{\sigma^1\},t)P(\{\sigma^q\};t), \tag{6}$$

where

$$\{\sigma^1\}=(\sigma_1,\ldots,\sigma_j,\sigma_{j+1},\ldots,\sigma_L),$$
$$\{\sigma^2\}=(\sigma_1,\ldots,\sigma_j+1,\sigma_{j+1},\ldots,\sigma_L),$$
$$\{\sigma^3\}=(\sigma_1,\ldots,\sigma_j+2,\sigma_{j+1},\ldots,\sigma_L), \tag{7}$$
$$\{\sigma^4\}=(\sigma_1,\ldots,\sigma_j+1,\sigma_{j+1}+1,\ldots,\sigma_L),$$
$$\{\sigma^5\}=(\sigma_1,\ldots,\sigma_j+2,\sigma_{j+1}+2,\ldots,\sigma_L),$$
$$\{\sigma^6\}=(\sigma_1,\ldots,\sigma_j+1,\sigma_{j+1}+2,\ldots,\sigma_L),$$
$$\{\sigma^7\}=(\sigma_1,\ldots,\sigma_j+2,\sigma_{j+1}+1,\ldots,\sigma_L).$$

The addition on the spin variables in the definition of the different states is to be understood as an operation in the cyclic group $(-1,0,1)$. $w_j(\{\sigma^p\}\to\{\sigma^q\},t)$ denotes the transition probability from a state $\{\sigma^p\}$ to a state $\{\sigma^q\}$ at time t. Its value is then either zero or positive.

Consider now that σ_{i+1} to $\sigma_{i+\ell}$ are given a certain value σ^*, not necessarily the same for each site, and let us sum over all the other variables. The result

$$P_\ell(t)=\sum_{\sigma_1=\pm1,0}\cdots\sum_{\sigma_i=\pm1,0}\sum_{\sigma_{i+\ell+1}=\pm1,0}\cdots\sum_{\sigma_N=\pm1,0}P((\sigma_1,\ldots,\sigma^*_{i+1},\ldots,\sigma^*_{i+\ell},\ldots,\sigma_N);\tau) \tag{8}$$

is the probability of existence of a particular cluster of size ℓ. If we assume translational invariance, this probability becomes the coverage of the chain by such clusters. In the particular case $\ell=1$, we get the fraction of sites of the lattice, which are in a certain state.

Applying these operations to the master equation, one derives a hierarchy of evolution equations for the probabilities $P_\ell(t)$. In the following sections, we will construct the explicit form of w_j appropriate for each scheme and then derive the corresponding hierarchy of equations for clusters of particles.

IV. SCHEME (1): STEPPED DESORPTION

The reaction between A particles is similar to the two-species systems studied previously [10], and so there should

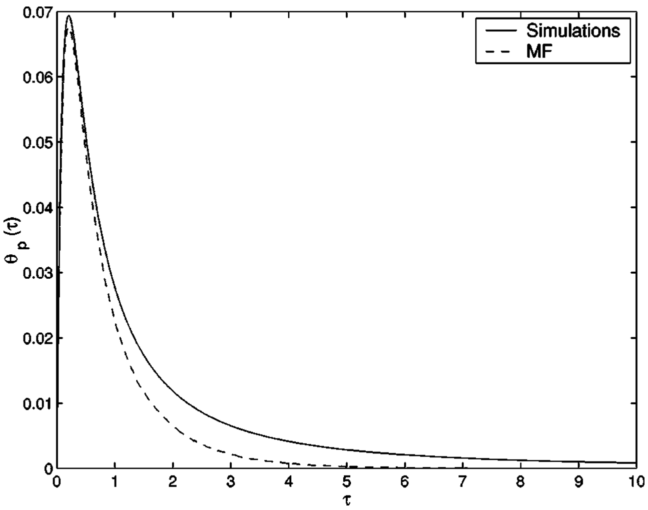


FIG. 2. Transient coverage of the lattice by P particles in scheme (1a) with $\epsilon = 0.1$. The difference between MF behavior and numerical simulations is due to the proximity conditions imposed on reactions between A particles that produce the P particles. In the asymptotic time limit, there are no P particles left on the lattice.

be no difference between the evolution equations for cluster of A particles in two- and three-species models. This allows one to test models (6) and (7) on a well-known case. As there is no proximity condition on the desorption of P particles, the coverage of the lattice in P particles converges towards the MF behavior. On the other hand, P particles appear from reactions between A particles, whose behavior is not MF like. The transient occupation of the lattice by P particles is thus different from that predicted by the MF equations, as shown in Fig. 2. The main question is then whether our model will reproduce this transient behavior.

A. Partial desorption

We associate species A, P, and S to the spin states $\sigma = 0,1$, and -1, respectively. The two events are thus represented by the transition probabilities $w_j(\{\sigma^1\} \rightarrow \{\sigma^2\},t)$ and $w_j(\{\sigma^3\} \rightarrow \{\sigma^1\},t)$ in the notation of Eqs. (7), all the other terms of the master equation being zero. The master equation (6) can thus be reduced to

$$\frac{dP(\{\sigma^1\};t)}{dt} = -\sum_j w_j(\{\sigma^1\} \rightarrow \{\sigma^2\},t) P(\{\sigma^1\};t) + \sum_j w_j(\{\sigma^3\} \rightarrow \{\sigma^1\},t) P(\{\sigma^3\};t). \tag{9}$$

The transition probabilities take the form

$$w_j^{12} = w_j^{31} = \frac{k_1}{2}(\sigma_j^2 - 1)(\sigma_{j+1}^2 - 1) + \frac{k_2}{2}\sigma_j(\sigma_j + 1), \tag{10}$$

where k_1, k_2 are the rate constants associated to the two steps (1a) and we introduced the abbreviated notation $w_j(\{\sigma^p\} \rightarrow \{\sigma^q\},t) = w_j^{pq}$. From now on, we will absorb the rate k_1 in the dimensionless time variable $\tau = k_1 t$ and we define the ratio of the two rates as $\epsilon = k_1/k_2$.

1. Dynamics of clusters of A particles

We are interested in the probability that ℓ contiguous sites are occupied by A particles:

$$P_\ell^A(\tau) = \sum_{\sigma_1 = \pm 1,0} \cdots \sum_{\sigma_i = \pm 1,0} \sum_{\sigma_{i+\ell+1} = \pm 1,0} \cdots \sum_{\sigma_N = \pm 1,0} P((\sigma_1, \ldots, \sigma_{i+1} = 0, \ldots, \sigma_{i+\ell} = 0, \ldots, \sigma_N);\tau).$$

Performing this operation on Eq. (9), one has

$$\frac{dP_\ell^A(\tau)}{d\tau} = \sum_{j \neq i+1, \ldots, i+\ell} \sum_{\sigma_j = \pm 1,0} -w_j(\{\sigma^1\} \rightarrow \{\sigma^2\},\tau) P(\{\sigma^1\};\tau) + w_j(\{\sigma^3\} \rightarrow \{\sigma^1\},\tau) P(\{\sigma^3\};\tau). \tag{11}$$

In the second term of this equation, performing the change of variables $\sigma^3 = \sigma^1$ for the initial state of the transition probability implies that $\sigma^1 = \sigma^2$ in the final state, changing this term to $w_j(\{\sigma^1\} \rightarrow \{\sigma^2\},\tau) P(\{\sigma^1\};\tau)$. This causes a cancellation of the two terms for all j, except for those belonging to the subset $j = i+1, \ldots, i+\ell$. Furthermore, since $\sigma_j = 0$ for this subset, the second term of Eq. (11) is 0. Let us also note that, in the remaining evolution equation, the second term vanishes because $w_j(\sigma + 2) = 0$ if $\sigma = 0$. We will now evaluate the nonvanishing contributions for the relevant values of j:

(1) For $j = i+1$, the contribution of the site reads

$$\begin{aligned} C_1 &= -(\sigma_{i+1}^2 - 1)(\sigma_{i+2}^2 - 1) \\ &\quad \times P_R(\sigma_{i+1} = 0, \sigma_{i+2} = 0, \ldots, \sigma_{i+\ell} = 0) \\ &= -P_\ell^A(\tau), \end{aligned} \tag{12}$$

where we used the notation

$$P_R(\sigma_a, \ldots, \sigma_{a+b}) = \sum_{j = \pm 1,0; j \neq a, a+1, \ldots, a+b} P(\{\sigma^p\}).$$

(2) For $j = i+\ell$, the contribution of the site reads

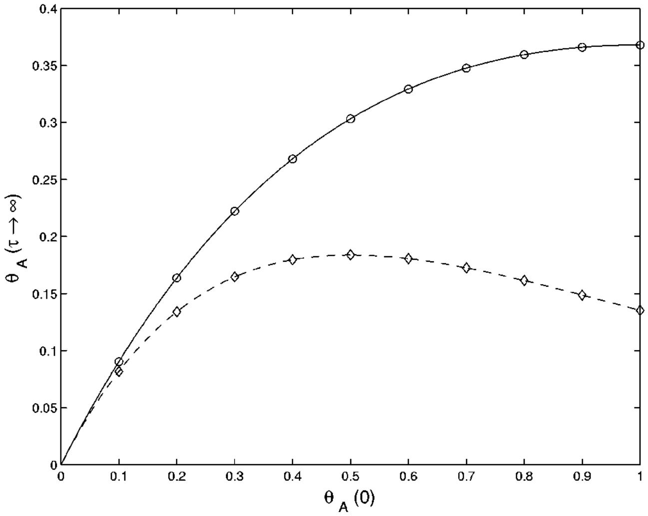


FIG. 3. Dependence of the global asymptotic coverage in A particles on the initial condition. The solid line corresponds to the partial desorption and the slashed one to the full desorption. The bullets and diamonds represent the numerical values given by microscopic simulations of the partial and full desorptions, respectively.

$$C_2 = -\sum_{\sigma_{i+\ell+1}=\pm 1,0} (\sigma_{i+\ell}^2 - 1)(\sigma_{i+\ell+1}^2 - 1) \times P_R(\sigma_{i+1}=0,\dots,\sigma_{i+\ell}=0,\sigma_{i+\ell+1}) = \sum_{\sigma_{i+\ell+1}=\pm 1,0} (\sigma_{i+\ell+1}^2 - 1)$$

$$P_R(\sigma_{i+1}=0,\dots,\sigma_{i+\ell}=0,\sigma_{i+\ell+1}) = -P_R(\sigma_{i+1}=0,\dots,\sigma_{i+\ell+1}=0) = -P_{\ell+1}^A(\tau). \tag{13}$$

For the full subset, we have one contribution of the type C_2 corresponding to the reaction between sites $i+\ell$ and $i+\ell+1$ and $\ell-1$ contributions of the type C_1 corresponding to reaction between sites $i+1$ and $i+2$, $i+2$ and $i+3,\dots,i+\ell-1$ and $i+\ell$. Finally, the evolution equation (11) reduces to

$$\frac{dP_\ell^A(\tau)}{d\tau} = -[(\ell-1)P_\ell^A(\tau) + P_{\ell+1}^A(\tau)]. \tag{14}$$

This equation is similiar to the one found for direct partial desorption [10] and which was solved by Majumdar and Privman [18]. For $\ell=1$, the probability represents the coverage of the lattice by A particles and its solution

$$P_\ell^A(\tau) = (P_1^A)^\ell(0)\exp[-(\ell-1)\tau - P_1^A(0)(1-e^{-\tau})] \tag{15}$$

fits very well the Monte Carlo simulations, as can be seen in Fig. 3.

2. Dynamics of clusters of P particles

We define P_ℓ^P as the probability that ℓ contiguous sites are occupied by homologous P particles,

$$P_\ell^P(t) = \sum_{\sigma_1=\pm 1,0} \cdots \sum_{\sigma_i=\pm 1,0} \sum_{\sigma_{i+\ell+1}=\pm 1,0} \cdots \sum_{\sigma_N=\pm 1,0} P((\sigma_1,\dots,\sigma_{i+1}=1,\dots,\sigma_{i+\ell}=1,\dots,\sigma_N);t).$$

We will restrict ourselves in the quantity P_1^P, the coverage of the lattice in P particles. From the previous equation, we obtain for the evolution of P_1^P,

$$\frac{dP_1^P(\tau)}{d\tau} = \sum_{\sigma_{i+2}=\pm 1,0} (\sigma_{i+1}^2 - 1)(\sigma_{i+2}^2 - 1)P(\sigma_{i+1}=0,\sigma_{i+2}) - \frac{1}{2\epsilon}\sigma_{i+1}(\sigma_{i+1}+1)P(\sigma_{i+1}=1),$$

$$\frac{dP_1^P(\tau)}{d\tau} = P_2^A(\tau) - \frac{1}{\epsilon}P_1^P(\tau). \tag{16}$$

Since the form of $P_2^A(\tau)$ is known, the evolution equation for this quantity reduces to an inhomogeneous differential equation that can be solved. The result is

$$P_1^P(\tau) = \frac{[P_1^A(0)]^{a+2}}{a!} e^{-(\tau/\epsilon) - P_1^A(0)} \times \left[e^{P_1^A(0)e^{-\tau}} \sum_{n=1}^{a} (n-1)! \frac{e^{n\tau}}{[P_1^A(0)]^n} - e^{P_1^A(0)} \times \sum_{n=1}^{a} \frac{(n-1)!}{[P_1^A(0)]^n} \mathrm{Ei}(P_1^A(0)e^{-\tau}) + \mathrm{Ei}(P_1^A(0)) \right] + P_1^P(0)e^{-\tau/\epsilon}, \tag{17}$$

where $a=(1-\epsilon)/\epsilon$. We compare this expression with the results of simulations in Fig. 4. To achieve this result, we used the following relation:

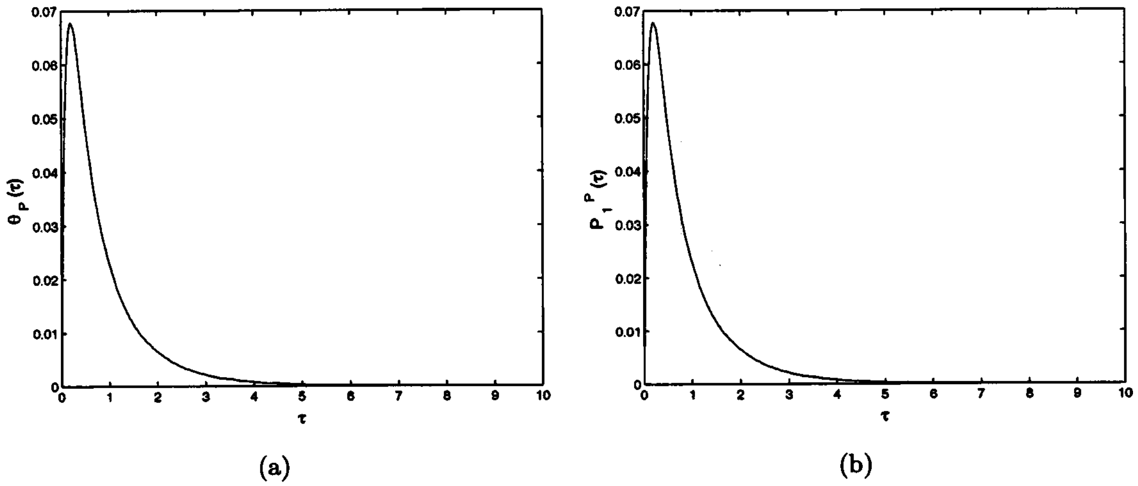


FIG. 4. Transient coverage by P particles for scheme (1a), with $\epsilon=0.1$. (a) shows numerical results while the analytical result given by Eq. (17) is plotted in (b).

$$\int \exp(at+be^{-t})dt=\frac{b^a}{a!}\left[\exp(be^{-t})\sum_{n=1}^{a}(n-1)!\frac{e^{nt}}{b^n}-\mathrm{Ei}(be^{-t})\right],$$

provided a is a positive integer. Although this limitation is nonphysical, there is a wide range of values for k_1 and k_2 which satisfy this condition. It does not therefore induce a real loss of generality for our solution.

B. Full desorption

This scheme is similar to the previous one with the difference that two A particles transform into products P at the same time. The P particles desorb as before. The master equation reduces now to

$$\frac{dP(\{\sigma^1\};t)}{dt}=-\sum_j w_j(\{\sigma^1\}\to\{\sigma^4\},t)P(\{\sigma^1\};t)+\sum_j w_j(\{\sigma^5\}\to\{\sigma^1\},t)P(\{\sigma^5\};t), \tag{18}$$

and the transition probabilities take the form

$$w_j^{14}=w_j^{51}=k_1(\sigma_j^2-1)(\sigma_{j+1}^2-1)+\frac{k_2}{2}\sigma_j(\sigma_j+1). \tag{19}$$

The computations are very similar to those presented for the partial desorption so we just present the results. We obtain for the evolution of a cluster of A particles:

$$\frac{dP_\ell^A(\tau)}{d\tau}=-[(\ell-1)P_\ell^A(\tau)+2P_{\ell+1}^A(\tau)], \tag{20}$$

the solution of this equation being

$$P_\ell^A(\tau)=(P_1^A)^\ell(0)\exp[-(\ell-1)\tau-2P_1(0)(1-e^{-\tau})]. \tag{21}$$

The accuracy of the prediction is quite good, as seen in Fig. 3. For the coverage of the lattice by P particles, we get the following evolution equation:

$$\frac{dP_1^P(\tau)}{d\tau}=2P_2^A(\tau)-\frac{1}{\epsilon}P_1^P(\tau), \tag{22}$$

whose solution is

$$\begin{aligned}P_1^P(\tau)=&\frac{[2P_1^A(0)]^{a+2}}{2a!}e^{-(\tau/\epsilon)-2P_1^A(0)}\\&\times\left[e^{2P_1^A(0)e^{-\tau}}\sum_{n=1}^{a}(n-1)!\frac{e^{n\tau}}{[2P_1^A(0)]^n}-e^{2P_1^A(0)}\right.\\&\left.\times\sum_{n=1}^{a}\frac{(n-1)!}{[2P_1^A(0)]^n}\mathrm{Ei}(2P_1^A(0)e^{-\tau})+\mathrm{Ei}(2P_1^A(0))\right]\\&+P_1^P(0)e^{-\tau/\epsilon},\end{aligned} \tag{23}$$

where $a=(1-\epsilon)/\epsilon$.

V. SCHEME (2)

We now turn to the reaction $A+B\xrightarrow{k_1}S+S$. We assign the value $\sigma_j=1$ to a site occupied by an A particle, $\sigma_j=-1$ to a site occupied by a B particle, and $\sigma_j=0$ to a free site S. As previously, some of the terms of the master equation are zero, leading to

$$\begin{aligned}\frac{dP(\{\sigma^1\};t)}{dt}=&-\sum_j\,[w_j(\{\sigma^1\}\rightarrow\{\sigma^6\},t)\\&+w_j(\{\sigma^1\}\rightarrow\{\sigma^7\},t)]P(\{\sigma^1\};t)\\&+\sum_j\,w_j(\{\sigma^6\}\rightarrow\{\sigma^1\},t)P(\{\sigma^6\};t)\\&+\sum_j\,w_j(\{\sigma^7\}\rightarrow\{\sigma^1\},t)P(\{\sigma^7\};t).\end{aligned}\tag{24}$$

In the notation of Eqs. (7), the reaction $A+B\rightarrow S+S$ is represented by the probabilities w^{17} and w^{61}, while w^{71} and w^{16} correspond to the reaction $B+A\rightarrow S+S$. This distinction is necessary by our assumption that a particle on a site j can react only with its right-hand neighbor $j+1$. The explicit form of the transition probabilities are

$$w_j^{16}=w_j^{71}=\frac{k_1}{4}\sigma_j(\sigma_j-1)\sigma_{j+1}(\sigma_{j+1}+1),\tag{25}$$

$$w_j^{17}=w_j^{61}=\frac{k_1}{4}\sigma_j(\sigma_j+1)\sigma_{j+1}(\sigma_{j+1}-1).\tag{26}$$

Again, we will absorb the reaction rate k_1 in the dimensionless time variable $\tau=k_1t$.

A. Definition of reactive clusters

We are interested in the probability that an ℓ-site cluster is "fully reactive." In particular, let $P_\ell^A(\tau)$ be the fraction of ℓ-site clusters which are entirely filled with reactants in the configuration $ABAB\cdots$. Similarly, let $P_\ell^B(\tau)$ be the fraction of ℓ-site clusters with configuration $BABA\cdots$. We will make the distinction between clusters with an even number of sites and ones with an odd number of sites, although it will be shown that this does not have any effect on the final results. We have the following definitions:

$$P_\ell^{A(even)}(\tau)=\sum_{\sigma_1=\pm1,0}\cdots\sum_{\sigma_i=\pm1,0}\sum_{\sigma_{i+\ell+1}=\pm1,0}\cdots\sum_{\sigma_N=\pm1,0}P((\sigma_1,\ldots,\sigma_{i+1}=1,\sigma_{i+2}=-1,\ldots,\sigma_{i+\ell}=-1,\ldots,\sigma_N);\tau),$$

$$P_\ell^{B(even)}(\tau)=\sum_{\sigma_1=\pm1,0}\cdots\sum_{\sigma_i=\pm1,0}\sum_{\sigma_{i+\ell+1}=\pm1,0}\cdots\sum_{\sigma_N=\pm1,0}P((\sigma_1,\ldots,\sigma_{i+1}=-1,\sigma_{i+2}=1,\ldots,\sigma_{i+\ell}=1,\ldots,\sigma_N);\tau).$$

The definitions for odd-sized clusters are similar to those for even-sized ones, except for the state of lattice site $\sigma_{i+\ell}$, which will be 1 for $P_\ell^{A(odd)}$ and -1 for $P_\ell^{B(odd)}$. As before, $P_1^A(\tau)$ is the coverage of the lattice by A particles and likewise $P_1^B(\tau)$ for B particles. We will now derive the evolution equations for these quantities from Eq. (24).

B. Dynamics of reactive clusters

The evolution equation for $P_\ell^A(\tau)$, for ℓ even or odd, is

$$\begin{aligned}\frac{dP_\ell^A(\tau)}{d\tau}=&\sum_{j\neq i+1,\ldots,i+\ell}\;\sum_{\sigma_j=\pm1,0}[-[w_j(\{\sigma^1\}\rightarrow\{\sigma^6\},\tau)\\&+w_j(\{\sigma^1\}\rightarrow\{\sigma^7\},\tau)]\\&\times P(\{\sigma^1\};\tau)+w_j(\{\sigma^6\}\rightarrow\{\sigma^1\},\tau)P(\{\sigma^6\};\tau)\\&+w_j(\{\sigma^7\}\rightarrow\{\sigma^1\},\tau)P(\{\sigma^7\};\tau)].\end{aligned}\tag{27}$$

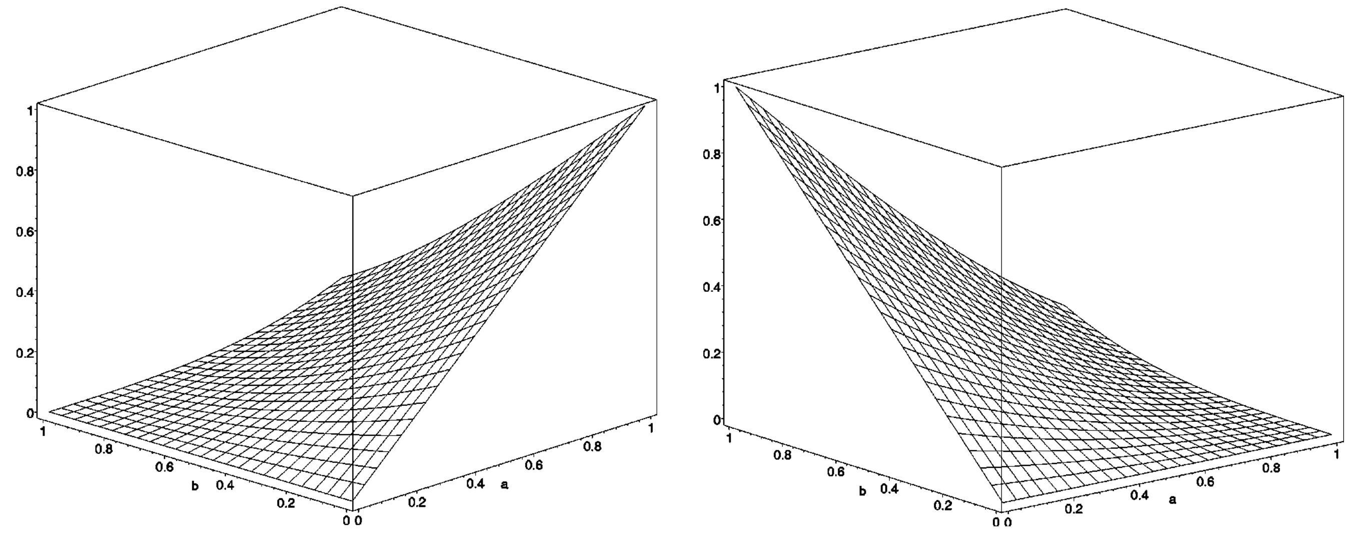
As in Sec. IV A 1, a proper change of variables will cause a cancellation of terms for all j except those belonging to the subset $j=i,\ldots,i+\ell$. For example, let us have a look at the third term of the equation, $w_j(\{\sigma^6\}\rightarrow\{\sigma^1\},\tau)P(\{\sigma^6\};\tau)$. A change of variable $(\sigma_j,\sigma_{j+1})\rightarrow(\sigma_j+2,\sigma_{j+1}+1)$ or, in the notation of Eqs. (7) $\sigma^1\rightarrow\sigma^7$, changes it to $w_j(\{\sigma^1\}\rightarrow\{\sigma^7\},\tau)]P(\{\sigma^1\};\tau)$, so that it cancels with the second term of Eq. (27). Likewise, a change of variable $(\sigma_j,\sigma_{j+1})\rightarrow(\sigma_j+1,\sigma_{j+1}+2)$ in $w_j(\{\sigma^7\}\rightarrow\{\sigma^1\},\tau)P(\{\sigma^7\};\tau)$ cancels it with the first term. Furthermore, we can already note that the contributions of the third and the fourth terms vanish because $w^{61}=w^{71}=0$ if $(\sigma_j,\sigma_{j+1})=(1,-1)$.

We will now evaluate the contributions for the set, assuming translational invariance:

(a) For $j=i$, the contribution of the site reads

$$\begin{aligned}C_1=&-\sum_{\sigma_i=\pm1,0}\frac{1}{4}\sigma_i(\sigma_i-1)\sigma_{i+1}(\sigma_{i+1}+1)\\&\times P(\sigma_i,1,-1,\ldots,\sigma_{i+\ell}=-1)\\&-\sum_{\sigma_i=\pm1,0}\frac{1}{4}\sigma_i(\sigma_i+1)\sigma_{i+1}(\sigma_{i+1}-1)\\&\times P(\sigma_i,1,-1,\ldots,\sigma_{i+\ell}=-1).\end{aligned}$$

The second term is clearly zero and the first one reduces to



(a) (b)

FIG. 5. Analytical estimation of the final coverage in (a) A and (b) B particles, plotted against the initial condition.

$$C_1=-\sum_{\sigma_i=\pm 1,0}\frac{1}{2}\sigma_i(\sigma_i-1)P(\sigma_i,1,-1,\dots,\sigma_{i+\ell}=-1)$$
$$=-P(-1,1,-1,\dots,-1)=-P^B_{\ell+1}.$$

It is easy to see that we get the same result with ℓ odd.

(b) For $j=i+1$, the contribution of the site reads

$$C_2=-P(\sigma_{i+1}=1,\sigma_{i+2}=-1,\dots,\sigma_{i+\ell}=-1)$$
$$\times\left[\frac{1}{4}\sigma_{i+1}(\sigma_{i+1}-1)\sigma_{i+2}(\sigma_{i+2}+1)\right.$$
$$\left.+\frac{1}{4}\sigma_{i+1}(\sigma_{i+1}+1)\sigma_{i+2}(\sigma_{i+2}-1)\right]=-P^A_{\ell}.$$

It is also clear in this case that we get the same contribution with ℓ odd.

(c) For $j=i+\ell$, the contribution of the site reads, for ℓ even,

$$C_3=-\sum_{\sigma_{i+\ell+1}=\pm 1,0}\frac{1}{4}\sigma_{i+\ell}(\sigma_{i+\ell}+1)\sigma_{i+\ell+1}$$
$$\times(\sigma_{i+\ell+1}-1)P(1,-1,\dots,-1,\sigma_{i+\ell+1})$$
$$-\sum_{\sigma_{i+\ell+1}=\pm 1,0}\frac{1}{4}\sigma_{i+\ell}(\sigma_{i+\ell}-1)\sigma_{i+\ell+1}$$
$$\times(\sigma_{i+\ell+1}+1)P(1,-1,\dots,-1,\sigma_{i+\ell+1})$$
$$=-\sum_{\sigma_{i+\ell+1}=\pm 1,0}\frac{1}{2}\sigma_{i+\ell+1}(\sigma_{i+\ell+1}+1)$$
$$\times P(1,-1,\dots,-1,\sigma_{i+\ell+1})=-P^A_{\ell+1}.$$

For ℓ odd, the contribution reads

$$C_3=-\sum_{\sigma_{i+\ell+1}=\pm 1,0}\frac{1}{4}\sigma_{i+\ell}(\sigma_{i+\ell}+1)\sigma_{i+\ell+1}$$
$$\times(\sigma_{i+\ell+1}-1)P(1,-1,\dots,1,\sigma_{i+\ell+1})$$
$$-\sum_{\sigma_{i+\ell+1}=\pm 1,0}\frac{1}{4}\sigma_{i+\ell}(\sigma_{i+\ell}-1)\sigma_{i+\ell+1}$$
$$\times(\sigma_{i+\ell+1}+1)P(1,-1,\dots,1,\sigma_{i+\ell+1})$$
$$=-\sum_{\sigma_{i+\ell+1}=\pm 1,0}\frac{1}{2}\sigma_{i+\ell+1}(\sigma_{i+\ell+1}+1)$$
$$\times P(1,-1,\dots,1,\sigma_{i+\ell+1})=-P^A_{\ell+1}.$$

Once again, there is no difference for the final result.

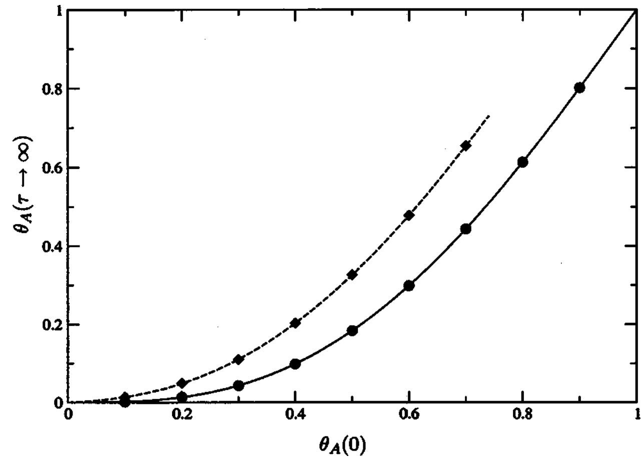


FIG. 6. Final coverage of the lattice in A particles, plotted against the initial condition $\theta_A(0)$ for the two-species desorption $A+B\rightarrow S+S$. The results displayed in this figure correspond to initial conditions $\theta_A(0)+\theta_B(0)=1$ [solid line for analytical result of Eq. (31); bullets for simulation results] and $\theta_A(0)+\theta_B(0)=0.75$ [dotted line for analytical result of Eq. (31); diamonds for simulation results].

TABLE I. Asymptotic existence of four-site A particle clusters and two-site B particle clusters, analytical versus numerical results.

Initial conditions		Analytical results		Numerical simulations	
θ_A	θ_B	A_4	B_2	C_{A4}	C_{B2}
0.3	0.7	1.192×10^{-3}	3.109×10^{-1}	1.200×10^{-3}	3.103×10^{-1}
0.5	0.5	2.299×10^{-2}	9.197×10^{-2}	2.310×10^{-2}	9.211×10^{-2}
0.8	0.2	3.141×10^{-1}	2.695×10^{-3}	3.144×10^{-1}	2.752×10^{-3}

For the full subset, we have one contribution of type C_1, one of type C_3, and $(\ell-1)$ of type C_2. The evolution equation (27) then reduces to

$$\frac{dP_\ell^A(\tau)}{d\tau}=-(\ell-1)P_\ell^A-P_{\ell+1}^A-P_{\ell+1}^B. \tag{28}$$

A similar derivation leads to

$$\frac{dP_\ell^B(\tau)}{d\tau}=-(\ell-1)P_\ell^B-P_{\ell+1}^B-P_{\ell+1}^A. \tag{29}$$

Majumdar and Privman [18] solve this system by combining the probabilities P_ℓ^A and P_ℓ^B as $P_\ell=\frac{1}{2}(P_\ell^A+P_\ell^B)$. This leads to

$$\frac{dP_\ell(\tau)}{d\tau}=-(\ell-1)P_\ell-2P_{\ell+1}. \tag{30}$$

This equation can be solved using the same ansatz as for the single-species desorption. We get the following expressions for the coverage of the lattice by A and B particles:

$$P_1^A(\tau)=\frac{1}{2}[P_1^A(0)-P_1^B(0)+(\rho+\omega)e^{-2\rho(1-e^{-\tau})}-(\rho-\omega)e^{2\rho(1-e^{-\tau})}], \tag{31}$$

$$P_1^B(\tau)=\frac{1}{2}[P_1^B(0)-P_1^A(0)+(\rho+\omega)e^{-2\rho(1-e^{-\tau})}-(\rho-\omega)e^{2\rho(1-e^{-\tau})}], \tag{32}$$

where $\omega=\frac{1}{2}(P_1^A(0)+P_1^B(0))$ and $\rho=\sqrt{P_1^A(0)P_1^B(0)}$.

These results are plotted for $\tau\to\infty$ in Fig. 5. In order to make comparisons with numerical simulations clearer, we take a section of Fig. 5(a) along initial conditions $P_1^A(0)+P_1^B(0)=1$ and $P_1^A(0)+P_1^B(0)=0.75$. This is represented in Fig. 6. As for schemes (1a) and (1b), these solutions fit very well the results of the numerical simulations.

C. Frozen clusters

One of the main features in $A+B$ desorption schemes is the formation of clusters of homologous particles, when diffusion is allowed, slowing down the reaction. In the absence of diffusion, the only such clusters remaining on the lattice are the ones initially present (possibly eaten up on their edges). Below we derive some exact results for these quantities, in both the asymptotic and the transient regimes.

We can write the probability that ℓ contiguous sites are occupied by A or B particles as follows:

$$A_\ell(\tau)=\sum_{\sigma_1=\pm1,0}\cdots\sum_{\sigma_i=\pm1,0}\sum_{\sigma_{i+\ell+1}=\pm1,0}\cdots\sum_{\sigma_N=\pm1,0}P((\sigma_1,\ldots,\sigma_{i+1}=1,\ldots,\sigma_{i+\ell}=1,\ldots,\sigma_N);t),$$

$$B_\ell(\tau)=\sum_{\sigma_1=\pm1,0}\cdots\sum_{\sigma_i=\pm1,0}\sum_{\sigma_{i+\ell+1}=\pm1,0}\cdots\sum_{\sigma_N=\pm1,0}P((\sigma_1,\ldots,\sigma_{i+1}=-1,\ldots,\sigma_{i+\ell}=-1,\ldots,\sigma_N);t).$$

The evolution equation for $A_\ell(\tau)$ is similar to Eq. (27), keeping in mind that the cluster is now different. Carrying out the same basic operations (change of variables, cancellation and zero contributions), we get the following evolution equation:

$$\begin{aligned}\frac{dA_\ell(\tau)}{d\tau}&=-\sum_{\sigma_i=\pm 1,0}\sum_{\sigma_{i+\ell+1}=\pm 1,0}(w_i^{16}+w_i^{17}+w_{i+\ell}^{16}+w_{i+\ell}^{17})P(\sigma_i,\sigma_{i+1}=1,\ldots,\sigma_{i+\ell}=1,\sigma_{i+\ell+1})\\&=-\frac{1}{2}\sum_{\sigma_i=\pm 1,0}\sigma_i(\sigma_i-1)P(\sigma_i,\sigma_{i+1}=1,\ldots,\sigma_{i+\ell}=1)\\&\quad-\frac{1}{2}\sum_{\sigma_{i+\ell+1}=\pm 1,0}\sigma_{i+\ell+1}(\sigma_{i+\ell+1}-1)P(\sigma_{i+1}=1,\ldots,\sigma_{i+\ell}=1,\sigma_{i+\ell+1})\\&=-P(\sigma_i=-1,\sigma_{i+1}=1,\ldots,\sigma_{i+\ell}=1)-P(\sigma_{i+1}=1,\ldots,\sigma_{i+\ell}=1,\sigma_{i+\ell+1}=-1).\end{aligned}$$

We assume that the particles are distributed randomly, so that $A_\ell(0)=A_1^\ell(0)$. We can use this to factorize the right-hand terms of the last equation

$$\begin{aligned}\frac{dA_\ell(\tau)}{d\tau}&=-P(\sigma_i=-1,\sigma_{i+1}=1)P(\sigma_{i+2}=1,\ldots,\sigma_{i+\ell}=1)\\&\quad-P(\sigma_{i+1}=1,\ldots,\sigma_{i+\ell-1}=1)\\&\quad\times P(\sigma_{i+\ell}=1,\sigma_{i+\ell+1}=-1).\end{aligned}$$

With translational invariance, this leads to

$$\begin{aligned}\frac{dA_\ell(\tau)}{d\tau}&=-P_2^B(\tau)A_{\ell-1}(0)-A_{\ell-1}(0)P_2^A(\tau)\\&=-A_{\ell-1}(0)(P_2^A(\tau)+P_2^B(\tau))\\&=A_{\ell-1}(0)\frac{dP_1^A(\tau)}{d\tau}.\end{aligned}$$

The solution is then easy to compute,

$$A_\ell(\tau)=P_1^A(\tau)A_{\ell-1}(0). \tag{33}$$

An identical derivation gives the following result for B clusters:

$$B_\ell(\tau)=P_1^B(\tau)B_{\ell-1}(0). \tag{34}$$

Table I shows the solutions of Eqs. (33) and (34) in the asymptotic time limit against the results of numerical simulations, for various initial conditions.

VI. CONCLUSION

We have developed a simple analytical model for the stochastic dynamics of three-state reactive schemes on low-dimensional support. As this dynamics is implemented through the transition probabilities w_j, the formalism is applicable to any lattice model, as long as the events affect one or two sites of the lattice. The formalism can be amended to account for reactive systems affecting more sites and/or involving a higher number of distinct species.

Two different models, stepped desorption and two-species desorption, which are two distinct generalizations of the two-state cooperative desorption presented in a previous work [10] have been considered here. In each case we derived from the master equation the evolution equations for clusters of particles, which allowed us to compute expressions for the lattice coverage by each species. These expressions fit with great accuracy the results of numerical simulations of the systems considered, both in the asymptotic time limit and the transient regime, as it has been shown in the case of particles in the stepped desorption.

Two-species cooperative desorption arises in many heterogeneous catalysis systems, where A and B may stand for the different reactants (e.g., carbon monoxide and atomic oxygen in the CO oxidation reaction on platinum surface). In order to be able to compare our models with real experiments some features have to be added, the main two being higher dimensionality of the support and reactant mobility. The latter problem has been adressed recently for single-species systems [19,20] and it is certainly worth a try to carry out with the present master equation formalism.

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