

Reaction-controlled cooperative desorption in a one-dimensional lattice: A dynamical approach

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The spinlike dynamics of immobile reactants in a one-dimensional lattice is analyzed for two representative systems involving cooperative desorption. An exact combinatorial approach is worked out. Its failure to reproduce the results of microscopic simulations is shown to be associated with the lack of sufficiently strong ergodic properties, as a result of which the final state depends strongly on the initial conditions. A dynamical approach to the problem based on the Master equation description is subsequently developed, leading to full agreement with the microscopic simulations.

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I. INTRODUCTION

Recently, there has been considerable interest in nonlinear phenomena that take place in sets of low dimensionality. The unexpected outcome of these investigations has been that in such diverse systems as interacting spins, random walk, aggregating particles, or chemical reactions, inhomogeneous fluctuations may induce substantial deviations of the macroscopic behavior from that predicted by the mean field (MF) approach. A crossover from dimension-dependent behavior at low dimensions to universal MF behavior at some critical dimension has also been identified and found to depend on both the characteristics of the lattice and the nature and degree of nonlinearity of the dynamics.

So far, most of the literature on the effect of dimensionality on the dynamics of reactive systems has focused on diffusion-controlled reactions [1,2]. Clearly, if the space where the reaction takes place is of low dimensionality, the number of neighbors and hence the effective mobility of the diffusing particles is low. As a result, some reactions may take place with difficulty or be even forbidden. On the other hand, in high space dimensionality each individual particle can reach and react with the other ones in the system, a necessary prerequisite for the validity of MF. This is at the origin of the deviations of the behavior of diffusion-controlled reactive systems from MF found in the recent literature.

In a series of papers, two of the present authors and co-workers have considered the opposite limit in which reactant mobility can be neglected within the time scale of interest, thereby focusing specifically on the role of reactive dynamics in the overall behavior. Nontrivial effects of space dimensionality have been found in this case as well, for the following types of kinetics:

(i) reactions $A + (n-1)X \rightleftharpoons nX$ ($n=2$ and 3) in a fully covered regular or fractal lattice under closed system conditions [3-5];

(ii) Schlögl reaction schemes under nonequilibrium (open system) conditions known to give rise in the MF limit to bifurcations toward multiple steady states [6,7];

(iii) a lattice generalization of the Lotka-Volterra model under nonequilibrium (open system) conditions [8].

In the first case and for $n=3$, starting from a configuration containing only X particles, the system stabilizes in 1D in a nonequilibrium, locally frozen asymptotic state in which the ratio of A to X particles is quite different from the MF ratio $r=1$. In the second case bifurcation was shown to be shifted or even suppressed altogether in low dimensions. Finally, in the third case the sustained oscillations predicted in the MF limit are suppressed in 1D but persist in 2D.

The origin of the above deviations lies in the existence of a hard core not allowing the reacting particles to be in the same lattice node, and of short range interactions as a result of which particles can react only with their immediate neighbors. The number of these neighbors depends on the coordination number of the lattice, and is small in low dimensions. As a result a reaction involving cooperative steps will proceed with difficulty in low-dimensional systems. Now, reactive dynamics amounts to the change of identity of the species involved. The progress of the reaction can therefore be monitored by a discrete, "color" or "spin"-like variable whose possible states equal the number of species involved. The color or spin propagation associated with the dynamics may, under certain conditions, behave analogously to diffusion although the origin of spatial propagation is quite different here than in the case of particle diffusion.

In the present paper we consider spinlike dynamics of immobile reactants in a 1D lattice in cases where the evolution does not involve a single ergodic set of states as in Ref. [3], but depends strongly on the initial conditions. The particular context in which this study will be implemented are nonlinear irreversible reactions associated with *cooperative desorption*,



popularly referred to, respectively, as "coagulation" and "annihilation." Here A denotes the reactive species and S the empty lattice site. In the mean-field limit both reactions

predict a trivial final state. Indeed, the rate equations associated with Eqs. (1a) and (1b) are, respectively,

$$\frac{dc}{dt} = -kc^2, \tag{2a}$$

$$\frac{dc}{dt} = -2kc^2, \tag{2b}$$

whose unique steady-state solution is $c_s=0$, with a decay law of the form

$$c(t) = \frac{c_0}{1 + c_0kt} \tag{3a}$$

for scheme (1a), and

$$c(t) = \frac{c_0}{1 + 2c_0kt} \tag{3b}$$

for scheme (1b), c_0 being the initial condition. We shall show that when these schemes are implemented on a 1D lattice one obtains a very different description dominated entirely by inhomogeneous fluctuations.

In Sec. II the steady-state coverage of the lattice by A particles, as given by a combinatorial approach is evaluated exactly. In Sec. III a microscopic simulation of systems (1a) and (1b) is carried out, showing that the results of the combinatorial approach are inadequate, notably because of the strong dependence on the initial coverage of the lattice. In Secs. IV and V, a theoretical interpretation of these results is developed for the two schemes, based on a master equation description of the evolution of the spinlike variables associated with the occupation of the lattice. This leads to a hierarchy of equations for the dynamics of clusters containing contiguous A particles. An exact solution of this hierarchy is carried out from which the role of initial conditions is clearly brought out, in full agreement with the results of the microscopic simulation. Finally, the main conclusions are drawn in Sec. VI.

II. STEADY-STATE COVERAGE: COMBINATORIAL APPROACH

We shall first calculate the time-independent probability distribution describing the coverage θ_A by A particles using combinatorial arguments. Clearly, starting from a fully covered lattice, the time-independent state of the system will be composed of sequences of free sites S , separated by isolated A particles. We hereafter consider the statistics of these sequences successively for the cases of cooperative partial and full desorption.

A. The cooperative partial desorption

Let n be the number of isolated A particles left in a lattice of size L , subjected to fixed boundary conditions. Starting from the uniform A configuration with a vacant site at each border, a time-invariant configuration is characterized by the fact that there must be at least one free site between two A particles. This restriction implies that at least $n-1$ sites of the lattice cannot be occupied by A particles. The number of

sites that can be filled by A particles is thus $L-(n-1)-2$. The number of different ways to put these n particles on these $L-n-1$ allowed sites is given by

$$M_L(n) = \binom{L-n-1}{n}.$$

The maximum number of A particles allowed for a lattice of fixed size L must satisfy the equation

$$n = L - n - 1,$$

which gives $n_{\max} = (L-1)/2$. Of more interest is the most probable value \bar{n}_L , obtained by maximizing $M_L(n)$,

$$\frac{\partial}{\partial n} \left(\frac{(L-n-1)!}{n!(L-2n-1)!} \right) = 0.$$

In the limit $L \rightarrow \infty$, $n \rightarrow \infty$ (n/L finite) one may use the Stirling approximation, yielding

$$\theta_A = \lim_{L \rightarrow \infty} \frac{\bar{n}_L}{L} = \frac{5 - \sqrt{5}}{10} = 0.2764. \tag{4}$$

This value practically coincides with the average number of A particles

$$\langle n \rangle_L = \frac{\sum_{n=0}^{(L-1)/2} n M_L(n)}{\sum_{n=0}^{(L-1)/2} M_L(n)},$$

normalized by L whose numerical evaluation yields

$$\theta_A = \frac{\langle n \rangle_L}{L} = 0.2763$$

for a lattice of size $L = 1001$.

B. The cooperative full desorption

Starting again from the fully covered configuration, the set of time-independent states is composed of sequences of the form

$$SSASSSSASSSSSS, \tag{5a}$$

$$S_2AS_2S_2AS_2S_2S_2. \tag{5b}$$

We wish to find the number $M_L(n)$ of different ways of putting n particles A in a 1D lattice of size L under these conditions. We have the following restrictions:

- (A) If L is odd (even), n must be odd (even).
- (B) We assume fixed boundary conditions [S_2 at the edges of Eq. (5b)].
- (C) The sequence (5a) can be rewritten in the form (5b) with a characteristic length $L' = n + (L-n)/2 = (L+n)/2$.
- (D) Between two A particles, there is at least one S pair. Thus $n-1$ sites of the lattice (5b) cannot be occupied by A particles.

In view of the above, the number of allowed sites for the A particles is

$$L' - (n-1) - 2 = \frac{L-n}{2} - 1,$$

and $M_L(n)$ is now given by

$$M_L(n) = \binom{(L-2-n)/2}{n}.$$

The maximum number of A particles allowed for a fixed size L must satisfy the equation

$$n = \frac{L-2-n}{2},$$

which gives $n_{\max} = (L-2)/3$. As for the most probable value \bar{n}_L , it is now given by

$$\frac{\partial}{\partial n} \left(\frac{[(L-2-n)/2]!}{n![(L-2-3n)/2]!} \right) = 0.$$

Using again the Stirling formula one obtains in the asymptotic limit

$$\theta_A = \lim_{L \rightarrow \infty} \frac{\bar{n}_L}{L} = 0.1770. \quad (6)$$

On the other hand, the average number of A particles in a chain of size L (odd) is

$$\langle n \rangle_L = \frac{\sum_{n=0, \text{odd}}^{(L-2)/3} n M_L(n)}{\sum_{n=0, \text{odd}}^{(L-2)/3} M_L(n)}.$$

The numerical evaluation for a size $L=902$ gives

$$\theta_A = \frac{\langle n \rangle_L}{L} = 0.1769,$$

which is nearly undistinguishable from the above result (6).

III. MICROSCOPIC SIMULATION

To derive the statistical properties of the asymptotic state we perform Monte Carlo simulations on a 1D lattice composed of L sites. The simulation algorithm, subsequently referred to as code A , is summarized by the following steps:

(1) An initial configuration containing a number n of A particles placed at random on the L sites is chosen, the initial coverage being $\theta_A(0) = n/L$. The extreme sites are set vacant to be consistent with the combinatorial analysis.

(2) At every Monte Carlo step, one lattice site i is selected at random.

(3) If the chosen lattice site i and a randomly chosen nearest neighbor j are occupied by A particles, then the reaction occurs with probability k . (a) The A particle on site i is transformed into S [reaction (1a)]. (b) The two A particles desorb and the sites i and j are vacated [reaction (1b)].

(4) In all other cases the lattice remains unchanged and the algorithm restarts at step 2 above.

The lattice chosen is composed of 2^{17} sites and each simulation is performed over 2×10^6 Monte Carlo steps. For

TABLE I. Asymptotic global coverage θ_A : simulation results.

	$A+A \rightarrow S+A$		$A+A \rightarrow S+S$	
Code A	0.3681 ^a	0.3033 ^b	0.1354 ^a	0.1842 ^b
Code B	0.3336 ^a	0.2915 ^b	0.1237 ^a	0.1802 ^b
Combinatorial	0.2764		0.1770	

^aStarting from an initial condition $\theta_A(0) \sim 1$.

^bStarting from an initial condition $\theta_A(0) = 0.5$.

simplicity we set $k=1$. Starting from a quasiuniform configuration in A (all sites are initially occupied by A particles except the two edges), for both reactions (1a) and (1b) the simulation gives a final global coverage which is significantly different from the predictions of the combinatorial analysis although the final configurations contain only isolated A particles. As shown in Table I, for the partial desorption the simulation result is larger than the expected one, while it is the contrary for the full desorption. One may wonder if this discrepancy is related to the algorithm used to check the occupation of a selected pair. To explore this we construct a slightly different code (code B) by changing step 3 [9]:

(3') If the chosen lattice i is occupied by A , the two nearest neighbors are checked in a random manner. If an A is found in any of them, the reaction occurs and we proceed as before.

Using code B , we note a shift of the simulation results but the discrepancy still persist, especially for reaction (1b). The sensitivity of the results towards the numerical code is *a priori* unexpected for such simple desorption schemes. It suggests that these systems do not possess strong ergodic properties leading to a mixing of the available states.

For reaction (1a) we have also analyzed the asymptotic behavior using a sequential algorithm (code C) starting from a quasiuniform configuration in A (sites 1 and L are vacant). Steps 2 and 3 differ from the previous code A in the following way:

(2'') At each Monte Carlo step, a new site i is chosen following the chain from $i=2$ to $i=L-1$.

(3'') One of the nearest neighbors j of the site i is chosen at random. If both sites are occupied by A , (a) The site i is vacated (code $C1$). (b) The site j is vacated (code $C2$). (c) The site i or the site j is vacated at random (code $C3$).

It is instructive to see how these different sequential codes perform on a small system of size $L=5$. The only allowed invariant states are

$$n=0: SSSSS,$$

$$n=1: SASSS \quad SSASS \quad SSSAS,$$

$$n=2: SASAS.$$

The probability of occurrence of $n=0, 1$, and 2 is thus respectively $1/5, 3/5$, and $1/5$. This leads to a theoretical mean coverage of 0.2 . By performing 10^5 realizations starting from the same initial configuration $SAAAS$, we obtain the statistical results summarized in Table II with a measured coverage of 0.3 . We note that the statistical weights of the different configurations are highly dependent on the numerical

TABLE II. Statistics of available configurations for a system of size $L=5$.

	Code C1	Code C2	Code C3
SSSSS			
SASSS		16.5%	6%
SSASS	16.6%	16.6%	25%
SSSAS	33.4%	16.8%	19%
SASAS	50%	50%	50%

code. This indicates that the 1D system is nonergodic in the space of available microscopic configurations.

For systems of $L \sim 10^3$, we have constructed the histogram of the global asymptotic coverage from 2×10^3 realizations starting from the same initial A uniform state using the codes A , B , and $C2$. As shown in Fig. 1 the simulation results clearly do not overlap with the theoretical distribution. We note also that the distributions obtained using the parallel code B and sequential code $C2$ are nearly indistinguishable but differ from the one constructed with code A .

We have also analyzed the dependence of the global asymptotic coverage on the initial condition $\theta_A(0)$ for both desorption reactions. As indicated in Table I (large system), for an initial coverage of 0.5 we note an improvement of the simulation results as compared to the combinatorial one. In this case the initial condition is chosen as a random repartition of $L/2$ A particles on the lattice and contains A clusters of various sizes separated by vacant sites. The chemical dynamics will destroy these clusters to give a configuration with only isolated A particles. Nevertheless, the fact that the state is initially mixed influences the observed asymptotic coverage. In other words, the imposed initial disorder is not spontaneously recovered starting from a uniform state. For smaller lattices ($L \sim 10^3$) the analysis of statistical properties reveals the same behavior. Figure 2 compare the histograms obtained starting from uniform and half coverages when using code A . When $\theta_A(0)=0.5$, the microscopic configuration is different from one realization to another but the distribution of final coverages shows the same shape as for the uniform case with a most probable value just shifted.

The results of the systematic study of the influence of the initial characteristics of the support are summarized in Fig. 3.

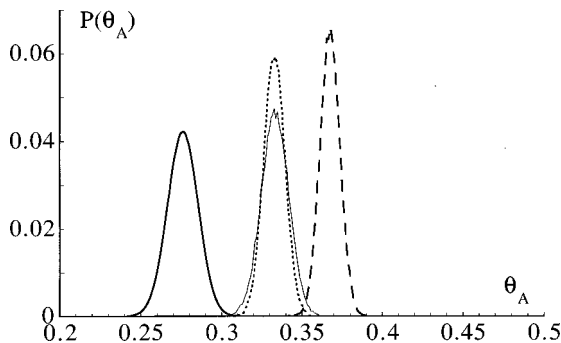


FIG. 1. Asymptotic distributions of global coverage for the cooperative partial desorption. The solid line corresponds to the combinatorial estimation. The histograms are generated by 5×10^4 realizations starting from a uniform A configuration. The dashed line is obtained using code A , the dotted one with code B , and the thin curve with a sequential algorithm ($C2$).

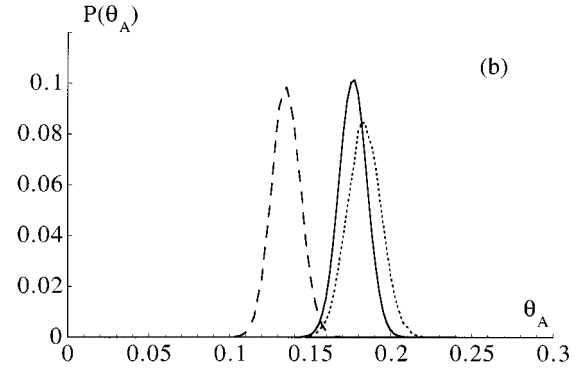
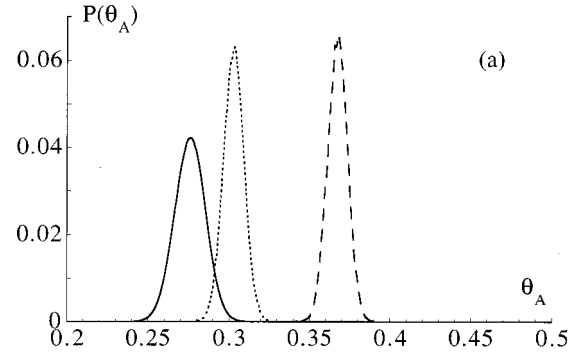


FIG. 2. Asymptotic distributions of global coverage for the cooperative partial desorption (a) and full desorption (b). The solid line is the theoretical probability given by the combinatorial estimation. The histograms are constructed using code A over 5×10^4 realizations for a lattice of size $L=1001$ in case (a) and $L=902$ in case (b). The dashed line corresponds to an initial uniform state [$\theta_A(0)=1$] and the dotted one to a random configuration characterized by the coverage $\theta_A(0)=0.5$.

We note that this dependence is reminiscent of a desorption isotherm. The curve presents a maximum in case (1b) and for $\theta_A(0)=0.5$ while it decreases continuously for reaction (1a). The strong influence of initial conditions on the final coverage further confirms the lack of ergodicity characterizing these desorption mechanisms. In the next two sections, we present a microscopic study that provides a theoretical framework for the unexpected numerical observations of this section.

IV. DYNAMICS OF THE COOPERATIVE PARTIAL DESORPTION

A. Model and master equation

We consider L spinlike variables $\sigma_i = \pm 1$ arranged on the sites of a 1D chain and standing, respectively, for a site occupied by an A particle ($\sigma=1$) and a vacant site ($\sigma=-1$). Starting from some arbitrary initial state, the evolution of the probability distribution $P(\{\sigma_j\}, t)$ of the set variables $\{\sigma\} = (\sigma_1 \cdots \sigma_j \cdots \sigma_L)$ with time is given by the Master equation [10]

$$\frac{dP(\{\sigma_j\}; t)}{dt} = - \sum_j w_j(\{\sigma\} \rightarrow \{\sigma'\}, t) P(\{\sigma\}; t) + \sum_j w_j(\{\sigma'\} \rightarrow \{\sigma\}, t) P(\{\sigma'\}; t), \quad (7)$$

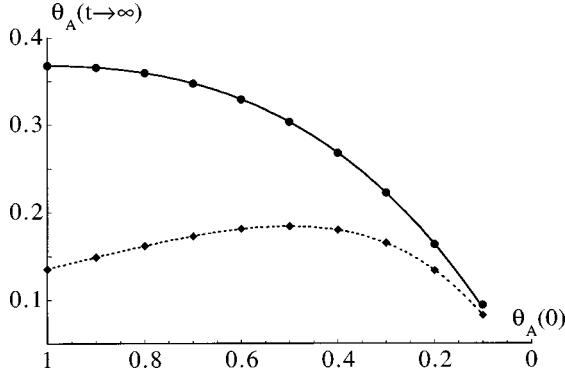


FIG. 3. Dependence of the global asymptotic coverage $\theta_A(t \rightarrow \infty)$ on the initial state characterized by $\theta_A(0)$. Each bullet represents the arithmetic mean value over 10 realizations for the partial desorption and each diamond for the full desorption. The system size is 2^{17} . The solid line corresponds to Eq. (15b) and the dotted one to Eq. (20) both in the long time limit.

where $\{\sigma'\}$ denotes the configuration $(\sigma_1 \cdots \sigma_j \cdots \sigma_L)$ and $w_j(\{\sigma\} \rightarrow \{\sigma'\}, t)$ represents the transition probability per unit time from the state $\{\sigma\}$ to the state $\{\sigma'\}$ at time t . It therefore introduces in the analysis the microscopic local laws specific to the system.

The explicit form of the transition probability for the model (1a) is obtained by requiring that in a site j the reaction proceeds if site j and one of its nearest neighbors selected at random are occupied by an A particle. This yields

$$w_j(\{\sigma\} \rightarrow \{\sigma'\}, t) = \frac{k}{8} (\sigma_j + 1)(\sigma_{j+1} + \sigma_{j-1} + 2). \quad (8)$$

This form corresponds to the numerical code A. Indeed, for a triplet $(\sigma_{j-1}, \sigma_j, \sigma_{j+1})$ in the state $(1, 1, -1)$ the transition probability for the site j is given by $w_j = k/2$. The factor $1/2$ stands for the probability of choosing one of the nearest neighbor sites. In contrast, in code B, this triplet will evolve to $(1, -1, -1)$ with probability k . In what follows we will absorb the rate k in the dimensionless time variable $\tau = kt$.

B. Dynamics of ℓ clusters

Let P_ℓ be the probability that ℓ connected sites are occupied by homologous A particles. In the framework of our formalism, this quantity can be written as

$$P_\ell(\tau) = \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_i = \pm 1} \sum_{\sigma_{i+\ell} = \pm 1} \cdots \sum_{\sigma_L = \pm 1} \times P[(\sigma_1 \dots \sigma_{i+1} = 1 \dots \sigma_{i+\ell} = 1 \dots \sigma_L); \tau].$$

Starting from Eqs. (7) and (8), one can easily derive the evolution equation for P_ℓ ,

$$\begin{aligned} \frac{dP_\ell(\tau)}{d\tau} &= \sum_j \sum_{\sigma_j = \pm 1, j \neq i+1, \dots, i+\ell} \\ &\times [-w_j(\{\sigma\} \rightarrow \{\sigma'\}, \tau) P(\{\sigma\}; \tau) \\ &+ w_j(\{\sigma'\} \rightarrow \{\sigma\}, \tau) P(\{\sigma'\}; \tau)]. \end{aligned} \quad (9)$$

By performing the change of variable $\sigma'_j = -\sigma_j$ in the second term, we observe a cancellation of the two terms for all j except those belonging to the subset $i+1, \dots, i+\ell$. For all sites of the subset, the second term of the right-hand side of Eq. (9) vanishes identically since the spin variable σ_j is set equal to one and $w_j(\{\sigma'\} \rightarrow \{\sigma\}, \tau) = 0$. We now evaluate the remaining contributions.

For $j = i+1$, the first term reads

$$\begin{aligned} & - \sum_{\sigma_i = \pm 1} \frac{1}{8} (\sigma_{i+1} + 1)(\sigma_i + \sigma_{i+2} + 2) \\ & \times P_R(\sigma_i, \sigma_{i+1} = 1 \cdots \sigma_{i+\ell} = 1) \\ & = -P_R(\sigma_i = 1, \sigma_{i+1} = 1 \cdots \sigma_{i+\ell} = 1) \\ & - \frac{1}{2} P_R(\sigma_i = -1, \sigma_{i+1} = 1 \cdots \sigma_{i+\ell} = 1) \end{aligned}$$

where

$$P_R(\sigma_i, \sigma_{i+1} = 1 \cdots \sigma_{i+\ell} = 1) = \sum_{\sigma_j = \pm 1, j \neq i, i+1, \dots, i+\ell} P(\{\sigma\})$$

Since

$$\begin{aligned} & P_R(\sigma_i = 1, \sigma_{i+1} = 1 \cdots \sigma_{i+k} = 1) \\ & + P_R(\sigma_i = -1, \sigma_{i+1} = 1 \cdots \sigma_{i+k} = 1) = P_\ell, \end{aligned}$$

the above relation takes the form

$$-P_{\ell+1} - \frac{1}{2}(P_\ell - P_{\ell+1}) = -\frac{1}{2}P_\ell - \frac{1}{2}P_{\ell+1}. \quad (10)$$

For $j = i+2$, the first term reduces to

$$\begin{aligned} & - \frac{1}{8} (\sigma_{i+2} + 1)(\sigma_{i+1} + \sigma_{i+3} + 2) P_R(\sigma_{i+1} = 1 \cdots \sigma_{i+\ell} = 1) \\ & = -P_\ell. \end{aligned} \quad (11)$$

Actually, we have two contributions of the type (10) corresponding to the edges of the cluster $j = i+1$ and $j = i+\ell$ and $\ell-2$ contributions of the type (11) corresponding to the sites $j = i+2, \dots, i+\ell-1$. Finally, Eq. (9) reduces to

$$\begin{aligned} \frac{dP_\ell(\tau)}{d\tau} &= -(\ell-2)P_\ell(\tau) - P_{\ell+1}(\tau) - P_\ell(\tau) \\ &= -(\ell-1)P_\ell(\tau) - P_{\ell+1}(\tau), \end{aligned} \quad (12)$$

which was previously obtained in an heuristic manner by Majumdar and Privman [11]. Since the initial configuration of the lattice is randomly filled with a given coverage p or, equivalently, with a given occupation probability per site, the initial probability of finding an ℓ cluster is given by

$$P_\ell(0) = p^\ell. \quad (13)$$

As shown in Ref. [11], a simple way to solve Eq. (12) is to use the ansatz

$$P_\ell(\tau) = c(\tau)[\sigma(\tau)]^{\ell-1}, \quad (14)$$

with $\sigma(0)=p$ and $c(0)=p$. Indeed, the solution (14) is possible provided

$$\frac{d\sigma}{d\tau} = -\sigma,$$

$$\frac{dc}{d\tau} = -\sigma c,$$

yielding

$$\sigma(\tau) = p \exp(-\tau), \quad (15a)$$

$$c(\tau) = p \exp[-p(1 - e^{-\tau})]. \quad (15b)$$

We notice that $P_1(\tau)=c(\tau)$ decreases in time but remains finite as $\tau \rightarrow \infty$. The quantity $P_{1,\infty}$ corresponds to the global asymptotic coverage of isolated A particles and is directly monitored in the simulations. An interesting feature is the explicit nonlinear dependence of the surviving reactant coverage on the initial density, even in the asymptotic limit,

$$P_{1,\infty} = e^{-1} = 0.368, \quad p = 1$$

$$P_{1,\infty} = \frac{1}{2} e^{-1/2} = 0.303, \quad p = 1/2.$$

As shown in Fig. 3 and Table II, the dependence in the initial density is in full agreement with the results of the microscopic simulations. All other probabilities $P_{\ell > 1}$ vanish asymptotically, meaning that all clusters containing more than one particle disappear sooner or later from the system. This is also confirmed by the simulations. It is worth noting that truncation of the infinite hierarchy (12) at a given order produces a formal expansion of the exact expression $P_{\ell,\infty}$ in powers of p , whose convergence is ensured only in the dilute limit.

V. DYNAMICS FOR THE COOPERATIVE FULL DESORPTION

A. Model and master equation

As previously, we consider L spinlike variables $\sigma_i = \pm 1$ arranged on the sites of a 1D chain. Starting from some arbitrary initial state, the evolution of the probability distribution $P(\{\sigma\}; t)$ of the set variable $\{\sigma\} = (\sigma_1 \cdots \sigma_j, \sigma_{j+1} \cdots \sigma_L)$ with time is given by the Master equation (7), where $\{\sigma'\} = (\sigma_1, \dots, -\sigma_j, -\sigma_{j+1}, \dots, \sigma_L)$. In other words, the main difference from the previous case is that both sites are affected by the reaction [12]. The transition probability now takes the form

$$w_j(\{\sigma\} \rightarrow \{\sigma'\}, t) = \frac{k_1}{4} (\sigma_i + 1)(\sigma_{i+1} + 1). \quad (16)$$

As before, the rate k will be absorbed in the adimensional time $\tau = kt$.

B. Dynamics of ℓ clusters

The definition of the reduced probability P_ℓ and its evolution equation (9) still hold for this reaction scheme. As in the preceding case, only the first term of Eq. (9) gives a nonvanishing contribution.

For $j=i$, the contribution reads

$$\begin{aligned} & - \sum_{\sigma_i = \pm 1} \frac{1}{4} (\sigma_i + 1)(\sigma_{i+1} + 1) \\ & \times P_R[(\sigma_i, \sigma_{i+1} = 1 \dots \sigma_{i+\ell} = 1); t] \\ & = - \frac{1}{2} \sum_{\sigma_i = \pm 1} (1 + \sigma_i) P_R[(\sigma_i, \sigma_{i+1} = 1 \dots \sigma_{i+\ell} = 1); t] \\ & = - P_{\ell+1}(t). \end{aligned} \quad (17)$$

For $j=i+1$, we have

$$\begin{aligned} & - \frac{1}{4} \sum_{\sigma_i = \pm 1} (\sigma_{i+1} + 1)(\sigma_{i+2} + 1) \\ & \times P_R[(\sigma_i, \sigma_{i+1} = 1 \dots \sigma_{i+\ell} = 1); t] \\ & = - \sum_{\sigma_i = \pm 1} P_R[(\sigma_i, \sigma_{i+1} = 1 \dots \sigma_{i+\ell} = 1); t] \\ & = - P_\ell(t). \end{aligned} \quad (18)$$

Here, we have two contributions of the type (17) corresponding to the reaction between sites $(i, i+1)$ and $(i+\ell, i+\ell+1)$ and $\ell-1$ contributions of type (18) corresponding to the reactions between sites $(i+1, i+2) \cdots (i+\ell-1, i+\ell)$. The evolution equation reduces then to

$$\frac{dP_\ell(t)}{dt} = -(\ell-1)P_\ell(t) - 2P_{\ell+1}(t). \quad (19)$$

This equation can be solved using the same method as in Sec. IV. The solution for single particles is

$$P_1(\tau) = p \exp[-2p(1 - e^{-\tau})], \quad (20)$$

leading to survival expectancies

$$P_{1,\infty} = e^{-2} = 0.135, \quad p = 1$$

$$P_{1,\infty} = \frac{1}{2} e^{-1} = 0.184, \quad p = 1/2.$$

These results are confirmed by the simulations (see Table II and Fig. 3).

VI. CONCLUSIONS

We have identified a mechanism of failure of MF description in low-dimensional systems, associated with the lack of ergodicity of the invariant state. More specifically, the invariant probability is not defined on a single ergodic set of states, but can be decomposed into a large (exponentially growing with size) number of states, each of which remains invariant under the dynamics. The relative weight of each of these configurations depends on the initial condition, and

thus explains the strong dependence of the results of our analysis on the initial coverage of the lattice.

Cooperative desorption arises in many heterogeneous catalysis-related problems, where A may stand for the reactive, atomic form of an otherwise practically inert substance A_2 (e.g., atomic nitrogen N versus N_2 in the NO/H_2 reaction on Pt). In this respect, therefore, the results reported in this paper are typical of a whole class of systems. On the other hand, they are limited by our simplifying assumption of the reactant being immobile. Incorporating mobility should, in principle, allow for an A particle to come eventually to the immediate neighborhood of another A particle, even if initially they were both surrounded by empty sites. Our scheme can be adapted to allow for this possibility by noting that the transition $\{\sigma_1, \dots, \sigma_j, \sigma_{j+1}, \dots, \sigma_L\} \rightarrow \{\sigma_1, \dots, -\sigma_j, -\sigma_{j+1}, \dots, \sigma_L\}$ (Sec. V) includes the possibility $(1, -1) \rightarrow (-1, 1)$ and $(-1, 1) \rightarrow (1, -1)$. These are precisely happening in diffusion to the right $[(1, -1) \rightarrow (-1, 1)]$ and to the left $[(-1, 1) \rightarrow (1, -1)]$. It would certainly be worth seeing whether this suffices to establish ergodicity in one dimension.

Future work in this area should also aim at allowing for more than one reactive species in the lattice. Taking also into account the empty sites, this would lead to a problem in which each lattice point can be in at least three possible states. Such “spin one,” or higher problems, have recently attracted attention in the literature [2,13] and are certainly worth tackling from the standpoint of the Master equation formalism.

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