Nonlinear Chemical Dynamics in Low Dimensions: An Exactly Soluble Model

A. Provata,[1] J. W. Turner,[1] and G. Nicolis[1]

Restricting space to low dimensions can cause deviations from the mean-field behavior in certain statistical systems. We investigate, both numerically and analytically, the behavior of the chemical reaction $A + 2X \rightleftharpoons 3X$ in one and two dimensions. In one dimension, we produce exact results showing that the trimolecular reaction system stabilizes in a nonequilibrium, locally frozen, asymptotic state in which the ratio r of A to X particles is a constant number, $r = 0.38$, quite different from the mean-field ratio, $r_{MF} = 1$. The same trimolecular model, however, reaches the mean-field limit in two dimensions. In contrast, the bimolecular chemical reaction $A + X \rightleftharpoons 2X$ is shown to agree with the mean-field predictions in all dimensions. For both models, we show that the adoption of certain types of transition rules in the laws of evolution can lead to oscillatory steady states.

1. INTRODUCTION

It is widely accepted that the dimensionality of the space in which statistical systems are embedded plays an important role in the evolution of their macroscopic properties. A considerable amount of work in areas such as spin systems,[1] random walks,[2] aggregation problems,[3] chemical reactions,[4] etc., has been devoted to the search for the role of dimensionality in the dynamical evolution. For all these systems it has been shown that there exists a critical value d_c above which the general features of the systems are independent of their dimensionality. However, below this critical dimension d_c, the macroscopic (and statistical) behavior becomes highly specific.

[1] Faculté des Sciences and Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles, Campus Plaine, C.P. 231, 1050 Bruxelles, Belgium.

1195

Spatial constraints play an important role in the dynamics of chemical reactions.[4] The atoms participating in the process usually have a finite range of interaction and so they can only react with a finite number of other atoms in their immediate neighborhood. If the space where the reaction takes place has low dimensionality, the number of neighbors as well as the mobility of the atoms are low. Consequently, some of the reactions take place with difficulty or are even forbidden. On the other hand, a high space dimensionality permits higher mobility, so each individual atom effectively can reach and react with all the other atoms in the system. It may thus be expected that for certain reactions, the phenomenological mean-field predictions will fail for sufficiently low dimensions.

Several investigators[5] have recently reported results on the failure of classical reaction kinetics in low-dimensional systems and fractal sets, principally as a result of the formation of macroscopic clusters. In the present paper we introduce a more microscopic modeling of the reaction process itself. We also focus more specifically on the thermodynamic aspects in connection with the ergodicity and mixing properties and the existence of an equilibrium state. Two examples of chemical reactions manifesting the role of low dimensionality in this respect are considered. In Section 2 we study the trimolecular chemical reaction $A + 2X \rightleftharpoons 3X$, which eventually amounts to the Schlögl model without input.[4,6] We first consider a one-dimensional lattice filled up with X particles, and show, both analytically and numerically, that the steady-state behavior is distinctly different from the phenomenological behavior apparent in higher dimensions. In Section 3, we show that if one adopts a particular set of transition rules in the laws of evolution of the trimolecular reaction system, the steady state becomes oscillatory with period 2. In Section 4, we study the bimolecular chemical reaction $A + X \rightleftharpoons 2X$ and show that already in one dimension this reaction shows mean-field behavior in the steady state. Comparison of the bimolecular and trimolecular reaction models shows that the critical dimension d_c is not universal, but depends on the particular type of the process. In Section 5, we discuss the effects of random initial conditions in the formation of the asymptotic state. Finally, we conclude by discussing other features of reactions in one and two dimensions, such as ergodicity, the role of diffusion, and higher-order processes.

2. THE TRIMOLECULAR REACTION MODEL $A + 2X \rightleftharpoons 3X$

We consider the trimolecular reaction model[4,6]

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \qquad\qquad (1)$$
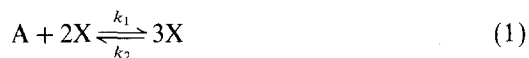
We stipulate that particles of type A, characterized by a "color" variable denoted for simplicity also by A, can change their color whenever they feel the presence of two particles of type X. Similarly, particles of type X can change their color, turning into A particles, when they are in the range of interaction of two other X particles. In (1), k_1 and k_2 represent the forward and backward reaction rates, respectively.

This reaction model is easy to realize in one dimension. The simplest version consists of particles A and X occupying the sites of a one-dimensional lattice, one particle per lattice site, with either periodic or fixed boundary conditions. To simplify further the model, we first assume that there are no vacant sites on the lattice and thus diffusion of the particles does not take place. (We will discuss the effects of diffusion in Section 6.) Since real molecules behave at very short distances like hard spheres, i.e., they can not pass through each other, we do not allow permutations of neighboring particles on the lattice during the system evolution. Furthermore, in view of the assumption that the reacting molecules have a finite range of interaction, we arrange the lattice constant (distance of two neighbor lattice sites) to be equal to the range of interaction of the reacting species. Under this condition, we can limit ourselves to nearest-neighbor interactions so that an A particle surrounded on the left and right by X particles can change its color, turning into an X particle. Similarly, an X particle "sandwiched" between two other X particles can change its color, turning into an A particle. [It is easy to visualize the A particles as having two active sites (•–•), thus needing two nearest-neighbor X particles in order to react and change color. A similar argument can be given for the X particles.]

For the time evolution of the system, we use the Markovian assumption. To secure its validity, we choose the time step so small that only one reaction can happen at every time step. The algorithm works as follows: (1) we choose one lattice site at random, (2) if the particle on the chosen site is surrounded by two X particles in the immediate neighborhood, it changes its color; otherwise the color on the chosen site is maintained.

It should be mentioned here that the above-defined system is not ergodic. For example, the uniform configuration which contains only A particles is obviously frozen. A necessary condition for the dynamical evolution of a site is the existence of X particles in the neighborhood. Similarly, for a random initial configuration which contains islands of A particles and islands of X particles, it is easy to see that the islands of A particles of size larger than one site will remain frozen, whereas the islands of X particles of size larger than two sites will give birth to A particles. It is thus advisable to understand first the evolution of a uniform configuration containing initially only X particles before we study the most general problem of random initial conditions.

Traditionally, in the study of chemical systems one resorts to a phenomenological description involving the local densities of particles A and X. The evolution in time of these densities $A(x, t)$ and $X(x, t)$, respectively, is given by[4,6]

$$\frac{dA(x, t)}{dt} = -k_1 A(x, t) X^2(x, t) + k_2 X^3(x, t) \tag{2}$$

$$\frac{dX(x, t)}{dt} = +k_1 A(x, t) X^2(x, t) - k_2 X^3(x, t) \tag{3}$$

where k_1 and k_2 denote the reaction rates in (1). Here we do not include the usual diffusion terms since the lattice is filled with particles that cannot move due to the hard-core potential. For equal reaction rates $k_1 = k_2$, Eqs. (2) and (3) admit in the long-time limit an equilibrium steady state in which the densities of the two species are equal, $A(x, t) = X(x, t)$. [There is also the trivial solution $X(x, t) = 0$, which is valid if we start with an initial configuration of only A particles.] The phenomenological description is independent of the dimensionality of space and coincides with the mean-field description. However, as we explained earlier, spatial effects which could change severely the behavior of the chemical system are neglected in the mean-field approach. In the remainder of this section, we show that the spatial restriction in one dimension leads the chemical reaction (1) to a nonequilibrium locally frozen state $\langle A(x, t) \rangle \neq \langle X(x, t) \rangle$ even in the case of equal reaction rates $k_1 = k_2$.

A one-dimensional system initially filled up with X particles can make transitions only to a certain number of states permitted by the given reaction rules and the requirement that at each step only one reaction can happen (Markovian assumption). The number of distinct allowed configurations also depends on the size of the system L. In the following analysis we will consider fixed boundary conditions mainly for two reasons: (a) to facilitate the calculations, since fixed boundary conditions produce fewer allowed configurations and (b) after the generalization to random initial conditions the islands of X particles will be intersected by islands of A particles and will thus be subjected to fixed boundaries.

As an example, for a system of size $L = 5$ with fixed boundary conditions, the only allowed states are

$$\begin{array}{ccccc}
X & X & X & X & X \\
X & A & X & X & X \\
X & X & A & X & X \\
X & X & X & A & X \\
X & A & X & A & X
\end{array}$$

In particular, it is obvious that states with two or more A particles next to each other, such as X A A X X, are not allowed by the dynamics. This suggests that the one-dimensional system in addition to being nonmixing is also nonergodic in the full state space of 2^{L-2} possible permutations of A and X.

The dynamics of the transitions between the allowed states of the system is described by the transition matrix T. The element T_{ij} represents the probability of transition from the state i to the state j. The mechanism for obtaining the elements of the transition matrix for a system of size L is the following:

1. Choose with probability $1/(L-2)$ any of the $L-2$ intermediate sites of the chain, excluding the edges.
2. If the chosen site is surrounded by two X particles, a transition to a state j takes place and so the matrix element is $T_{ij} = 1/(L-2)$.
3. When all possible transitions of the state i have been calculated the probability of no transition, represented by the element T_{ii}, can be calculated as $T_{ii} = 1 - \sum_{\text{all transitions}} (1/(L-2))$.

The transition matrix T is a doubly stochastic matrix with the sum of rows and columns equal to 1 and for the case $L = 5$ studied earlier takes the form

$$T = \begin{pmatrix} 0 & 1/3 & 1/3 & 1/3 & 0 \\ 1/3 & 1/3 & 0 & 0 & 1/3 \\ 1/3 & 0 & 2/3 & 0 & 0 \\ 1/3 & 0 & 0 & 1/3 & 1/3 \\ 0 & 1/3 & 0 & 1/3 & 1/3 \end{pmatrix} \tag{4}$$

The general form of the transition matrix T for arbitrary lattice size L is rather complicated, but here we give some general characteristics. For every state that has at least one particle A we have the possibility to stay at the same state. So all the diagonal elements, except the $(1, 1)$ element, will be nonzero. From every state with n_A particles A we can have a transition to states with $n_A \pm 1$ particles A. Because of that, the T matrix will have a block form with blocks of zero and nonzero elements. The blocks in general need not be square. On each line all the nonzero elements will have equal size except the diagonal element, but the sum of all elements on every line must be equal to one since the total probability is conserved in time. These general characteristics do not allow us to predict the exact form of the matrix for any value of the system size L, but they are sufficient to determine the behavior of the steady state.

The Frobenius theorem warrants that any stochastic matrix has a maximum eigenvalue equal to 1, which corresponds to the steady state of the system. The corresponding eigenvector has the form $(1, 1, 1, 1, 1)$, indicating that all the particular states contribute with the same weight in the formation of the steady state. From this point of view the system is ergodic in its allowed state space. As we show presently, this ergodicity condition does not warrant that at the steady state $\langle A(x, t) \rangle = \langle X(x, t) \rangle$.

Let us denote by $M_L(n)$ the number of different ways of putting n particles A in a 1D lattice of size L. If all possible configurations were allowed, then $M_L(n)$ would be equal to the combinatorial factor $\binom{L}{n}$. However, starting from the uniform X configuration and because of the Markovian assumption, we must leave one X particle between two A particles in the lattice. This restriction indicates that at least $(n-1)$ sites on the lattice cannot be occupied by A particles. If we also assume fixed boundary conditions, there are only $L - (n-1) - 2$ sites that can be filled by A particles. So the average number of A particles in a chain of size L with fixed boundary conditions can be estimated as

$$\langle A \rangle_L = \sum_{n=0}^{[(L-1)/2]} n \binom{L-n-1}{n} \Big/ \sum_{n=0}^{[(L-1)/2]} \binom{L-n-1}{n} \tag{5}$$

and similarly for $\langle X \rangle_L$. We have calculated numerically the of ratio $r = \langle A \rangle_L / \langle X \rangle_L$ as a function of L from Eq. (5). Figure 1 shows r as a function of L. As $L \to \infty$, the average ratio of A to X particles approaches a value close to 0.38. This is quite different from the mean-field value $r_{MF} = 1$.

To confirm this argument, we performed a direct simulation of the trimolecular reaction on a 1D lattice, following the algorithm given earlier.
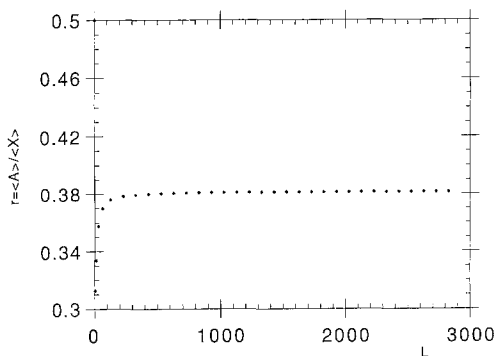

Fig. 1. Numerical evaluation of the ratio $r = \langle A \rangle / \langle X \rangle$ according to Eq. (5). As the system size L increases, the ratio r reaches an asymptotic value in the region of $r = (5 - \sqrt{5})/(5 + \sqrt{5})$.

In Fig. 2 we plot the ratio r as a function of time. We see that as time goes to infinity the trimolecular reaction approaches a steady state in which the ratio r takes the value $r = 0.38 \pm 0.02$. This result agrees with our previous argument.

We now give a rigorous derivation of the asymptotic value of r based on the properties of the quantity $M_L(n)$. It is easy to see that this quantity has the property

$$M_L(n) = M_{L-1}(n) + M_{L-2}(n-1) \tag{6}$$

Equation (6) holds because the allowed configurations containing n particles of color A in a chain of size L can be obtained by one of the following two ways: (a) either by adding one particle of color X to the left and of all the size-$(L-1)$ configurations with n particles of color A or (b) by adding the pair A–X to the left and of all the size-$(L-2)$ configurations which contain $(n-1)$ A particles. By summing both sides of Eq. (6) over the variable n, we can find the total number of allowed configurations for the different lattice sizes. The number of allowed configurations of a lattice of size L, $M_L = \sum_n M_L(n)$ has the Fibonacci property, namely

$$M_L = M_{L-1} + M_{L-2} \tag{7}$$

Let us now introduce the generating function for the quantity $M_L(n)$,

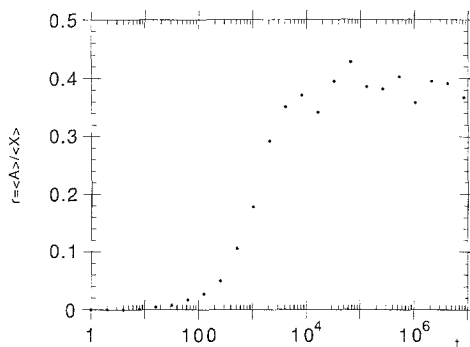$$P_L(\xi) = \sum_{n=0}^{\infty} M_L(n) \xi^n \tag{8}$$

Fig. 2. Numerical simulation of the chemical reaction $A + 2X \rightleftharpoons 3X$ (no diffusion). As time increases, the ratio $r = \langle A \rangle / \langle X \rangle$ approaches an asymptotic value in the region of 0.38 ± 0.02. The lattice size used in the simulation was $L = 2^{10}$ and the initial configuration contained only X particles and no vacant sites.

Notice that the quantity of interest $\langle A \rangle$ can be written as $\langle A \rangle = P'_L(\xi)/P_L(\xi)|_{\xi=1}$ and similarly for $\langle X \rangle$ and r. By introducing the generating function transformation into Eq. (6), we obtain

$$P_L(\xi) = P_{L-1}(\xi) + \xi P_{L-2}(\xi) \tag{9}$$

Furthermore, we introduce the winding number as

$$\omega_L(\xi) = \frac{P_L(\xi)}{P_{L+1}(\xi)} \tag{10}$$

By inserting Eq. (10) into Eq. (9) and taking the asymptotic limit $L \to \infty$ so that $\omega_L(\xi) = \omega_{L-1}(\xi) = \cdots$, we obtain ω as a function of ξ for large values of L,

$$\omega(\xi) = \frac{-1 + (1 + 4\xi)^{1/2}}{2\xi} \tag{11}$$

In terms of ω the quantity of interest $\langle A \rangle$ can be written as

$$\langle A \rangle = \left.\frac{P'_L(\xi)}{P_L(\xi)}\right|_{\xi=1} = -\left.\frac{\omega'(\xi)}{\omega(\xi)}\right|_{\xi=1} L, \qquad L \to \infty \tag{12}$$

This result combined with Eq. (11) leads to the asymptotic result

$$\langle A \rangle = \frac{5 - \sqrt{5}}{10} L, \qquad L \to \infty \tag{13}$$

and

$$r = \frac{\langle A \rangle}{\langle X \rangle} = \frac{5 - \sqrt{5}}{5 + \sqrt{5}} = 0.38 \cdots \tag{14}$$

as expected by the numerical simulation and the argument presented above.

The nonequilibrium state found in the trimolecular one-dimensional model is intrinsically different from the one found in open systems.[4] In an open chemical system the nonequilibrium steady state is caused by the continuous feeding of reactants. In low dimensions, however, owing to the conditions imposed by the geometry of the space, a nonequilibrium (frozen) asymptotic state is reached even in a closed system.

As we mentioned earlier, the mean-field equations (2)–(3) fail to describe the low-dimensional behavior in chemical reactions. Again the main point missing in the mean-field description is the element of the

geometry. To account for the effects of the geometry, we must modify the mean-field equations so that the rate constants will account for the allowed space configurations. In a crude approximation we can say that if we start from a uniform X configuration, at the steady state we have equal probability to obtain the following four neighborhood configurations: $C_1 = XXX$, $C_2 = AXX$, $C_3 = XAX$, and $C_4 = XXA$. Other neighborhood configurations are not allowed. From those four configurations the ratio of A to X particles would then be $r' = 3/9 = 0.333$. This is a very crude first approximation because we have neglected the shape and the structure of larger steady-state neighborhoods. These extra correlations that we have neglected will change the value of r' into the value given in Eq. (14). The geometry restrictions may be implemented by hand in Eqs. (2)–(3), at least at the steady state. For example, the left-hand side of Eq. (2) is zero (steady state), when the frequency of finding neighborhood configurations C_1 is three times smaller than the frequency of finding the other three neighborhood configurations. Thus, it is enough to require that $k_2 = 3k_1$ in Eqs. (2)–(3) in order to take into account the geometry restrictions in one dimension. This modification might have some sense in the steady state, but it is ambiguous with regard to the time-dependent behavior of the system.

3. OSCILLATORY SOLUTIONS

The rules governing the evolution of the trimolecular model introduced in Section 2 allowed for the possibility of no transition. Specifically, at every time step we choose with equal probability any site at random. If the particle at the chosen site is allowed to react by changing color, then the system changes state, whereas if transition is not favored by the neighbors, then the system remains at the current state. As we have seen, these evolution rules lead to a doubly stochastic transition matrix and consequently to a unique steady state. We now consider the following slight modification of the evolution rules. At every time step we keep track of the states to which a given state can evolve. We stipulate that the system must leave its current state, and assign equal probabilities to each allowed transition. This modification introduces a certain forcing in the model, which for this reason will be refered to as the "forced trimolecular model."

Let us now examine the properties of the transition matrix of the modified trimolecular model. Since at each time step the system is forced to leave its current state, the number of particles A in the system will either increase or decrease by one unit. So the resulting state will belong to the ensemble of states that contain one A particle more or one less then the original state. This observation allows us to guess the form of the transition

matrix. As in the case of the original model, the transition matrix should consist of blocks of nonzero and zero elements. However, the diagonal elements here will vanish because the system is forced to change state at every time step. For example, the modified, forced transition matrix for the chain of size $L = 6$ is

$$T_f = \begin{pmatrix} 0 & 1/3 & 1/3 & 1/3 & 0 \\ 1/2 & 0 & 0 & 0 & 1/2 \\ 1 & 0 & 0 & 0 & 0 \\ 1/2 & 0 & 0 & 0 & 1/2 \\ 0 & 1/2 & 0 & 1/2 & 0 \end{pmatrix} \tag{15}$$

The block form is due to transitions between ensembles of states. Notice that the blocks which contain the diagonal elements are always zero. The matrix T_f is still stochastic, although no longer doubly stochastic. The Frobenius theorem predicts that this matrix also possesses a maximum eigenvalue equal to 1. However, for matrices that have the above block form the eigenvalues appear always in pairs; if λ is an eigenvalue of the matrix T_f, then $-\lambda$ is also an eigenvalue. Indeed, let Λ be the eigenvector that corresponds to the eigenvalue λ. The eigenvector Λ takes the form

$$\Lambda = \begin{pmatrix} \mathbf{A} \\ \mathbf{B} \\ \mathbf{C} \\ \mathbf{D} \\ \vdots \end{pmatrix} \tag{16}$$

where the $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$, $\mathbf{D}$,...., correspond to the blocks of the matrix T_f arranged according to alternating parity in the number of A particles. Now, consider the vector

$$\Lambda' = \begin{pmatrix} -\mathbf{A} \\ \mathbf{B} \\ -\mathbf{C} \\ \mathbf{D} \\ \vdots \end{pmatrix} \tag{17}$$

in which the vectors $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$, $\mathbf{D}$,....., occur with alternating sign. By applying the matrix T_f (which has itself a block form corresponding to the vectors

A, B, C, D,...) on the vector Λ', it is easy to see that Λ' is an eigenvector of the matrix T_f with an eigenvalue

$$T_f \Lambda' = -\lambda \Lambda' \tag{18}$$

This proves that the eigenvalues of the matrix T_f come always in pairs $\pm\lambda$. This result, together with the stochasticity of T_f, permits us to conclude that the value -1 is also an eigenvalue of the transition matrix. Thus the modified trimolecular model presents an oscillatory asymptotic state with period 2.

Another feature of the matrices $T_f(L)$ is that they always have real eigenvalues. Indeed, it can be shown that there always exists a similarity transformation which turns the above matrices into symmetric matrices. Furthermore, as we saw earlier, the trace of the matrices $T_f(L)$ is always zero. This, together with the property of pairing eigenvalues, warrants a zero determinant for all the systems that have an odd number of allowed states.

We note here that oscillations of the same type are seen in a one-dimensional nearest-neighbor random walk with a similar transition law and reflecting boundary conditions. Consider a random walker who can take either one step to the right with probability p_i or one step to the left with probability q_i at time step i, so that $p_i + q_i = 1$. The transition matrix for this type of process will have a form similar to that of Eq. (15), namely

$$T_{RW} = \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots & 0 & 0 \\ p_2 & 0 & q_2 & 0 & \cdots & 0 & 0 \\ 0 & p_3 & 0 & q_3 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & 0 & 1 & 0 \end{pmatrix} \tag{19}$$

With the same reasoning given for the matrix T_f, the matrix T_{RW} will also have an oscillatory asymptotic state. The other properties of $T_f(L)$, such as the vanishing of the trace and eigenvalues occurring in pairs and having real values, hold also for the matrices T_{RW}.

4. THE BIMOLECULAR REACTION MODEL A + X ⇌ 2X

We now consider the bimolecular reaction model in one dimension

$$A + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2X \tag{20}$$

The question that we would like to discuss is whether this bimolecular model shows mean-field behavior or instead admits a nonequilibrium frozen state in low dimensions. The more general question that we would like to address is whether the low-dimensional behavior is the same in all chemical reactions or whether every individual chemical reaction shows its own behavior.

For the evolution of the bimolecular reaction model (20) we follow a similar algorithm as in the trimolecular model. We start with a one-dimensional lattice of size L. As initial condition we consider a uniform configuration containing only X particles. At every time step (a) a site is chosen at random in the lattice and (b) if there is an X particle either on the left or on the right of the chosen site, then the chosen site changes its color.

Using the above-described algorithm we calculated numerically the ratio $r = \langle A \rangle / \langle X \rangle$ as a function of time. Our results are shown in Fig. 3. We note that as time goes to infinity this quantity attains its mean-field value $r_{t \to \infty} = r_{\mathrm{MF}} = 1$. In the bimolecular reaction model initial conditions have minor effects in the formation of the steady state. Unlike the tri-molecular model, the bimolecular one attains the same value of the ratio r even if we start from an initial state which contains any nonzero number of particles X. The only frozen configuration in the bimolecular model is thus the one which initially contains only A particles. All the other configurations are permitted and all of them, when used as initial configua-tions, will evolve to a final configuration such that $r_{t \to \infty} = 1$.
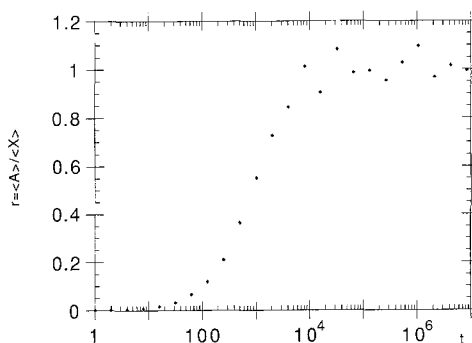

Fig. 3. Numerical simulation of the chemical reaction $A + X \rightleftharpoons 2X$ in one dimension, without diffusion. As time increases, the ratio $r = \langle A \rangle / \langle X \rangle$ approaches an asymptotic value of $r = 1 \pm 0.1$, which is in agreement with the mean-field results. The lattice size used in the simulations was $L = 1000$ and the same result was obtained starting with different initial concentrations of particles A and X.

This mean-field-type behavior of the bimolecular model in one dimension is easy to explain. Any initial cluster of A particles can be "eaten up" by the X particles which form the boundaries of the cluster. Since any configuration is allowed (except the uniform A configuration), the number of ways we can put n particles A on the lattice is equal to the number of ways we can put n particles X on the lattice. Namely, both of them are equal to $\binom{L}{n}$. Consequently, the ratio r is

$$r_{t \to \infty} = \frac{\sum_{n=0}^{L-1} n\binom{L}{n}}{\sum_{m=0}^{L} m\binom{L}{m}} = 1 - \frac{1}{2^{L-1}} = 1, \qquad L \to \infty \qquad (21)$$

It is now clear that the bimolecular model shows mean-field behavior even in one dimension, at least as far as the steady-state properties are concerned. Comparison between the two reaction models that we have considered show that the critical dimension d_c is not universal in chemical reactions but depends on the particular model. For the bimolecular model $d_c = 1$, whereas for the trimolecular model $d_c > 1$.

5. GENERAL INITIAL CONDITIONS

We have seen that the ergodicity properties are very different in the two reaction models examined here. The bimolecular system $A + X \rightleftharpoons 2X$ studied in Section 4 is ergodic over all the state space except for the state which consists entirely of A particles. This unique configuration is frozen and cannot be reached from any other configuration with the Markovian evolution rules adopted. In the classification of states familiar from Markov chains the state consisting entirely of A particles would qualify as a closed class consisting of a single absorbing state.

For the trimolecular model the anomalous ergodicity effect is magnified. As we have already mentioned, all the clusters larger than one site and entirely made out of A particles will remain frozen on the lattice, while regions between such clusters will evolve according to the results given in Section 2. So for the trimolecular model the state space is divided into many closed subspaces which do not communicated with each other.

The division of the state space into subspaces in the trimolecular model leads to different steady-state ratios r in each one of these subspaces. We have already found, in Section 2, the steady-state ratio r corresponding to the subspace containing the uniform X configuration. Let us now consider the most general random initial condition, of a chain of size L containing initially particles A with probability p and particles X with probability $q = (1 - p)$. For such a chain the probability to find an A

particle at the asymptotic state consists of two contributions: (a) the probability that the chosen particle belongs to one of the initial frozen A clusters, P_f; and (b) the probability that the chosen particle belongs to one of the nonfrozen, active clusters which contribute to the evolution, P_a.

The probability $P_f(s)$ that any particle belongs to a frozen cluster of size s is equal to $P_f(s) = sp^s(1-p)^2$, where the factor $(1-p)^2$ is needed to make sure that the cluster of A particles is interrupted by X particles at both ends.[7] Now the total probability P_f is

$$P_f = \sum_{s=2}^{\infty} sP_f(s) = \sum_{s=2}^{\infty} sp^s(1-p)^2 = p - p(1-p)^2 \tag{22}$$

In other words, the probability that a particle belongs to a frozen cluster is equal to the total probability of finding an A particle in the entire chain, minus the probability to find an isolated A particle cluster.

To find the probability for a particle to belong to an active cluster, one starts with a one-site nonfrozen cluster which contains an X particle and increases its length by adding either an A particle with probability p or an X particle with probability q. Equivalently, starting from a one-site cluster which which contains an A particle, one can increase its length only by adding an X particle with probability q. So if one wants to construct a cluster of length s starting from an initial X particle, it suffices to apply the transition matrix

$$\tau = \begin{pmatrix} q & q \\ p & 0 \end{pmatrix}$$

$(s-1)$ times on the initial state given by the column array $\binom{q}{0}$. The resulting column array, after we apply the τ matrix a number of times, will contain two elements: (a) the first element, $(1, 1)$, will correspond to the probability of a cluster starting and ending with an X particle, while (b) the $(2, 1)$ element will correspond to a cluster starting with an X particle and ending with an A particle. Since by construction the active clusters need to start and end with X particles, the probability to find such a cluster will be equal to the $(1, 1)$ element of the resulting column array. In a rigorous from we can write

$$\begin{pmatrix} Q_s \\ Q_s' \end{pmatrix} = \tau^{(s-1)} \begin{pmatrix} q \\ 0 \end{pmatrix} = \begin{pmatrix} q & q \\ p & 0 \end{pmatrix}^{(s-1)} \begin{pmatrix} q \\ 0 \end{pmatrix} \tag{23}$$

So the probability to find an active cluster of size s which starts and ends with X particles is

$$Q_s = \frac{q}{(q^2 + 4pq)^{1/2}} [\lambda_+^s - \lambda_-^s] \tag{24}$$

where $\lambda_\pm$ are the eigenvalues of the τ matrix

$$\lambda_\pm = \tfrac{1}{2}[q \pm (q^2 + 4pq)^{1/2}] \tag{25}$$

For a nonfrozen cluster containing a total of l particles a percentage $r_l' = \langle A \rangle_l / l$ of them will turn into A particles, where r_l' depends on the cluster size l. In particular, the values of r_l', $l = 1, 2,...$, can be found from the corresponding values of the ratio of A to X particles discussed in Section 2. We give here the first few values: $r_0' = r_1' = r_2' = 0$, $r_3' = r_4' = 1/6$, $r_5' = 1/5$, $r_6' = 5/24$, and $r_\infty' = r/(1 + r) = (5 - \sqrt{5})/10 = 0.276...$. Alternatively, we can express r_s' in terms of the generating function Q_s as

$$r_s' = \frac{1}{2s} \left[\frac{\partial Q_s}{\partial p} \middle/ Q_s \right]_{p = q = 1/2} \tag{26}$$

Consequently, the total probability to find an A particle at the final state starting from an initial random configuration in the limit of infinite system size, $L \to \infty$, is

$$p_A = \langle A \rangle / L = P_f + P_a$$

$$= p - (1 - p)^2 p + \lim_{L \to \infty} \sum_{s=1}^{L} r_s' s Q_s p^4, \qquad p \neq 0 \tag{27}$$

Here the factor p^4 in the last term of Eq. (27) assures that every nonfrozen region is bounded by four A particles, two on either side. By substituting Eqs. (25) and (26) into Eq. (27) we find the asymptotic density of A particles as

$$p_A = 2p^2 - p^3 + \frac{p^4}{4} \sum_{s=1}^{\infty} \left[-\frac{4}{5} + \frac{\sqrt{5}}{5} s \frac{\omega_+^{s-1} + \omega_-^{s-1}}{\omega_+^s - \omega_-^s} \frac{q}{(q^2 + 4pq)^{1/2}} \right] (\lambda_+^s - \lambda_-^s) \tag{28}$$

where

$$\omega_\pm = \frac{1 + \sqrt{5}}{4} \tag{29}$$

In the limit of $p = 1$ (only A particles initially on the lattice), the second and third terms on the right-hand side of Eq. (27) vanish. So the probability to find an A particle in the steady state is equal to $p_A = p = 1$, as expected.

In the limit of $p \to 0$ we set $p = \varepsilon$ and $q = 1 - \varepsilon$ and we expand Eq. (28) in terms of ε. In the limit of $\varepsilon \to 0$ we have

$$\lim_{p \to 0} p_A = \frac{\sqrt{5}}{10} \frac{1}{\omega_+} = \frac{5 - \sqrt{5}}{10} = r'_\infty \tag{30}$$

in agreement with our numerical simulations and the analytical results obtained in Section 2.

6. DISCUSSION

6.1. Diffusion Effects

It is rather interesting that the effects of diffusion are not very marked in the case of one-dimensional reactions. For example, in the trimolecular model, clusters of A particles with vacancies will not be destroyed. They can expand or shrink, but certainly cannot spontaneously create X particles, since, as before, the creation of an X particle requires the presence of other X particles in the neighborhood. Clusters of X particles with vacancies will create spontaneously A particles as before. The presence of vacancies is expected to slow down the approach toward the steady state, but is not expected to change much the essential features of the process, such as the appearance of nonequilibrium frozen states.

Consider the one-dimensional trimolecular model on a lattice of size L containing V vacancies and $L - V$ particles. Let us further suppose that we start from the particular configuration which contains only X particles and vacancies placed in such a way that the first $(L - V)$ sites are occupied by X particles and the remaining V sites are the vacant sites. The initial configuration will give rise to other configurations via the evolution rules explained in Section 2. The diffusion effect will result in splitting each one of these configurations into $\binom{L}{V}$ copies. In each of these copies the numbers of particles of A and X and of vacancies will be constant. So the ratio r of particles A to particles X at the steady state is not expected to change. If we denote again by $M_L(n)$ the number of ways we can put n particles of type A into a chain of size L with V vacancies, then

$$r_A^{\text{diff}} = \sum_{n=0}^{[(L-V-1)/2]} n M_L(n) \Big/ \sum_{n=0}^{[(L-V-1)/2]} M_L(n)$$

$$= \sum_{n=0}^{[(L-V-1)/2]} n M_{L-V}(n) \binom{L}{V} \Big/ \sum_{n=0}^{[(L-V-1)/2]} M_{L-V}(n) \binom{L}{V} \tag{31}$$

In the case of $L \to \infty$ and $V \to \infty$, with $L/V =$ finite, the value of r_A^{diff} is equal to the value of r_A, without diffusion.

In Fig. 4 we present results from a numerical simulation of the trimolecular reaction-diffusion model using the following algorithm: (a) start with an initial configuration of only X particles with a percentage $v\%$ of vacancies distributed randomly in between; (b) at every time step choose at random one site on the lattice; (c) decide at random if the particle on the chosen site will react or diffuse; (d) if in step (c) diffusion has been selected, the chosen particle will perform a nearest-neighbor random walk either to the left or to the right; if the nearest neighbors are occupied, the particle will remain on the current site; (e) if in step (c) reaction has been selected, then the chosen particle will change color if both nearest neighbors have color X; otherwise the chosen particle will retain the same color; (f) one time step is terminated and the algorithm restarts from step (b).

As seen in Fig. 4, the ratio r^{diff} of A to X particles approaches a value in the region of 0.38 ± 0.03 in the long-time limit comparable with Fig. 2 corresponding to the nondiffusive case.

It should be added that oscillating solutions do not exist if diffusion is included in the model. Even if the system is forced to leave its current state at every time step, diffusion can lead the system into a state with the same number of particles A and X as in the original state. Consequently, the blocks containing the diagonal elements of the transition matrix are not identically zero and the eigenvalues of the determinant do not appear in pairs.

A feature that has played an important role in our models is the assumption of hard-core interactions between the particles. If the diffusion
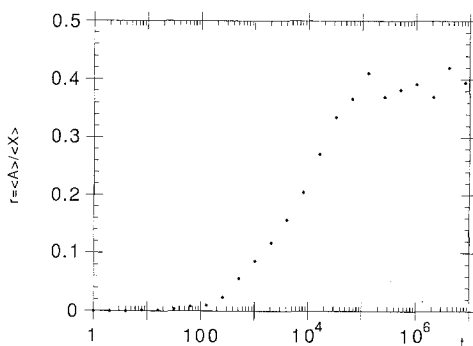

Fig. 4. Numerical simulation of the reaction-diffusion process $A + 2X \rightleftharpoons 3X$ in one dimension. The lattice size is $L = 2^{10}$ and it contains 40 % vacant sites. The asymptotic value of the ratio r is in the same region as in nondiffusive case (see Fig. 2).

process allows particles to go through each other, then mean-field results are obtained in all dimensions.[8] The reason for mean-field behavior is that clusters of A particles can be created or destroyed due to the diffusion of A particles through X regions.

6.2. Multimolecular Reactions and Reactions in Higher Dimensions

Consider the nearest-neighbor multimolecular reaction model of the form

$$A + jX \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (j+1)X, \qquad j = 1, 2,... \tag{32}$$
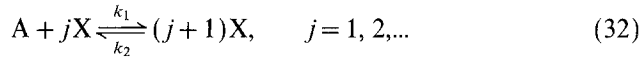
We expect that the critical dimension will depend on the value of j compared to the number of nearest neighbors. The latter is a function of the spatial dimension as well as of the lattice type (square lattice, triangular, octagonal, etc.). It is clear that when the number of nearest neighbors nn is less than j, the model is not well defined. When the number of nearest neighbors $nn = j$, as in the trimolecular reaction model in one dimension, then spatial efects play an important role and prohibit the appearance of mean-field behavior. Behavior different from mean field should appear in lattice types in which the number of nearesty neighbors is high enough so that the model can be well defined, but still low enough so that frozen regions could exist. For the square lattice, the number of nearest neighbors in d dimensions is $2d$. When $2d < j$ the nearest-neighbor interaction model is not well defined. For $j = d$ we have the critical dimension and for
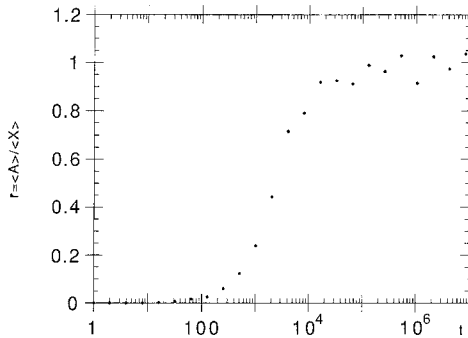

Fig. 5. Numerical simulation of the reaction $A + 2X \rightleftharpoons 3X$ in two dimensions. The square lattice used has size $2^5 \times 2^5$. In the long-time limit the ratio $r = \langle A \rangle / \langle X \rangle$ approaches the mean-field value $r = 1$.

$d \geqslant d_c = j$ the system shows mean-field behavior. In the intermediate region, $d < j \leqslant 2d$, the system presents non-mean-field behavior, as we have seen in the trimolecular nearest-neighbor reaction model in one dimension.

To confirm our conclusions about the behavior of the multimolecular model in higher dimensions, we performed numerical simulations of the trimolecular reaction model in a two-dimensional square lattice. In Figure 5 we plot the ratio r of A to X particles as a function of time. Figure 5 shows that as time increases, the ratio r reaches the value 1, which is the mean-field value. As expected, diffusion does not alter the mean-field results in two-dimensions.

ACKNOWLEDGMENTS

REFERENCES

1. S.-M. Ma, *Modern Theory of Critical Phenomena* (Benjamin, New York, 1976); H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).
2. W. Feller, *An Introduction to Probability Theory and Its Applications* (Wiley, New York, 1971); S. Havlin and D. ben-Avraham, *Adv. Phys.* **36**:695 (1987); G. H. Weiss and R. J. Rubin, *Adv. Chem. Phys.* **52**:363 (1983).
3. H. Takayasu, *Fractals in the Physical Science* (Manchester University Press, Manchester, 1990); T. Vicsek, *Fractal Frowth Phenomena* (World Scientific, Singapore, 1989); J. Feder, *Fractals* (Plenum, New York, 1988).
4. G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977); H. Malchow and L. Schimansky-Geier, *Noise and Diffusion in Bistable Nonequilibrium Systems* (B. G. Teubner Verlagsgesellschaft, 1985).
5. B. Chopard and M. Droz, *Europhys. Lett.* **15**(4):459 (1991); B. Chopard and M. Droz, *J. Stat. Phys.* **64**:859 (1991); K. Lindenberg, B. J. West, and R. Kopelman, in *Noise and Chaos in Nonlinear Dynamical Systems*, F. Moss, L. A. Lugiato, and W. Schleich, eds. (Cambridge University Press, Cambridge, 1990); K. Kang and S. Redner, *Phys. Rev. Lett.* **52**:955 (1984); K. Kang and S. Redner, *Phys. Rev. A* **32**:435 (1985); K. Lindenberg, W.-S. Sheu, and R. Kopelman, *J. Stat. Phys.* **65**:1269 (1991); C. R. Doering, M. Burschka, and W. Horsthemke, *J. Stat. Phys.* **65**:953 (1991); E. Clement, P. Leroux-Hugon, and L. M. Sander, *J. Stat. Phys.* **65**:925 (1991).
6. G. Nicolis and M. Malek Mansour, *Prog., Theor. Phys.* **64**:249 (1978); M. Malek Mansour, C. Van Den Broeck, G. Nicolis, and J. W. Turner, *Ann. Phys.* (N.Y.) **131**:283 (1981).
7. D. Stauffer, *Introduction to Percolation Theory* (Taylor & Francis, London, 1985).
8. D. Dab, A. Lawniczak, J.-P. Boon, and R. Kapral, *Phys. Rev. Lett.* **64**:2462 (1990); J. Weimar, D. Dab, J.-P. Bon, and S. Succi, *Europhys. Lett.*, submitted.