

Dynamics of Fluctuations in a Reactive System of Low Spatial Dimension

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We study, using master equation techniques, the time evolution of the average concentration and fluctuations in the two-species n -molecule reaction $A + (n-1)X \rightleftharpoons nX$ in one dimension described by a Glauber-type dynamical lattice model for the specific cases $n=2$ (bimolecular) and $n=3$ (trimolecular). The evolution is found to be quite different from that described by the Mean-Field equations even for the bimolecular case, where the steady state is mean-field. For the trimolecular process, the values of fluctuation correlations in the nonequilibrium steady state are well predicted by the fixed points of the dynamical equations obtained from the master equation. In addition, three-point fluctuation correlations are found to play an important role in both processes and are accounted for by an extended Bethe-type ansatz. The bimolecular system shows no memory effects of initial conditions, while the trimolecular system is characterized by memory effects in terms of the average concentration, fluctuations as well as the entropy. The spatial decay of fluctuation correlations is found to be short range at the steady state for the trimolecular system.

KEY WORDS: Low-dimensional systems; master equations; mean-field theory; nonequilibrium systems; nonlinear dynamics; chemical reactions.

1. INTRODUCTION

A large number of important physiochemical processes,⁽¹⁾ from heterogeneous catalysis to the reactivity of polymers, are found to occur in low-dimensional spaces. The crossover from lattice-dependent behavior at low dimensions to mean-field (MF) behavior at higher dimensions is an issue common to many different kinds of statistical systems, ranging from

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spin models⁽²⁾ to random walks⁽³⁾ and should therefore be of considerable interest to the field of reactive systems⁽⁴⁾ as well. This crossover occurs at a characteristic critical dimension d_u , commonly referred to as the upper critical dimension.

In recent work,⁽⁷⁾ the asymptotic steady state of the two species n -molecule process



has been studied simulationally for $n = 3$ using a lattice model and found to approach the mean-field one (i.e., containing an equal number of A and X particles) as the coordination number z of the lattice approaches 4. Thus, the upper critical dimension is here replaced by an upper critical coordination number that depends on n . The steady state in one dimension ($z = 2$) has in particular been observed⁽⁶⁾ to correspond to the equilibrium MF state for $n = 2$ (bimolecular), while for $n = 3$ (trimolecular), the system was found to freeze into a nonequilibrium state, described by a well-defined relative concentration of A and X particles. We emphasize that these bimolecular and trimolecular models are prototypes of a wide class of nonlinear stochastic processes, exhibiting quadratic and cubic nonlinearities, respectively. A study of their behavior is thus an important step toward a better understanding of the dynamics of these processes in general. The above crossover phenomenon can be viewed in the context of an interplay between lattice coordination number z and the degree of nonlinearity n .

Our aim in this paper is to study the dynamics of these systems and to explore the nature of correlations in the steady state. In particular, we will look at the asymptotic approach to equilibrium or to a nonequilibrium frozen state, as the case may be, and the evolution of fluctuations that describe the deviation from MF behavior for these processes. To this end, we shall adopt a master equation approach to obtain the dynamical equations that govern the evolution with time of the average concentration and the fluctuation correlations. We note that the birth-and-death master equation usually applied in the stochastic description of chemical reactions does not take into account the lattice geometry and is thus not appropriate for the purpose of this investigation. We believe that the formalism we develop here to study this crossover between MF and nonequilibrium behavior and the dynamics of the fluctuations that lead to it is very easily generalizable to the study of a wide variety of related problems.

The master equation approach we shall adopt for our lattice model is a variation on the one due to Glauber,⁽⁵⁾ originally proposed to analyze the dynamics of the one-dimensional Ising model. In Section 2 we

introduce this model and deduce explicitly the form of the transition probabilities by applying the local dynamical rules determined by the chemical process in question. We also derive the equations that describe the evolution with time of the average concentration and the correlations of the bimolecular and trimolecular processes in one dimension. These equations are not closed, as was found to be the case for those describing the corresponding quantities for the Ising model in ref. 5; one therefore needs to identify a valid truncation scheme to solve them. In Section 3 we identify such a truncation scheme and subsequently obtain a coupled set of equations for the average concentration and the fluctuation correlation between sites at distance n from each other. We discuss the solutions, the deviation from mean-field behavior for these processes, and the importance of three-point fluctuation correlations. The approach to equilibrium is found to be non-MF even for the bimolecular system, where the steady state is the same as that described by the MF equations.

In Section 4 we introduce a new scheme for solving the dynamical equations: this is also a hierarchical method, but does not involve truncation of fluctuations beyond some order. The first step of this hierarchy is in the spirit of the Bethe ansatz (we shall refer to it as "Bethe-type ansatz" in the rest of this work) and concentrates on two particles; we then extend the hierarchy to a larger number of particles while retaining all orders of fluctuation correlations between them. We find that the solution describes the behavior of the full bimolecular system substantially better than the truncation scheme of Section 3, due to the retention of higher order short-range fluctuation correlations, while neglecting long-range pair correlations.

Next in Section 5 we make some observations regarding the temporal relaxation behavior of the various quantities obtained from simulations. We also study the domain-size distribution and the related static and dynamic pattern entropies⁽⁸⁾ for an alternative view of the ordering and relaxation of the processes in question.

In Section 6 we investigate further the nature of the asymptotic steady state in terms of the spatial organization of the particles. We make use of the g -approximation⁽⁹⁾ to study further the nonequilibrium steady state for the trimolecular process, particularly the spatial decay of fluctuation correlations.

The main conclusions are drawn in Section 7.

2. THE MODEL

Consider a set of N spinlike variables $\sigma_i = \pm 1$ arranged on the sites i of a one-dimensional chain or ring. Starting from some arbitrary initial state,

the evolution of the probability distribution $P(\{\sigma\}; t)$ of the set variables $\{\sigma\} = (\sigma_1, \dots, \sigma_j, \dots, \sigma_N)$ with time is described by the master equation⁽⁵⁾

$$\begin{aligned} \frac{dP(\{\sigma\}; t)}{dt} = & -\sum_j w_j(\{\sigma\} \rightarrow \{\sigma'\}, t) P(\{\sigma\}; t) \\ & + \sum_j w_j(\{\sigma'\} \rightarrow \{\sigma\}, t) P(\{\sigma'\}; t) \end{aligned} \quad (2)$$

where we denote by $\{\sigma'\}$ the state $(\sigma_1, \dots, -\sigma_j, \dots, \sigma_N)$ 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 : thus its value is always either zero (when the reaction is not allowed) or positive (proportional to the rate of the reaction). Furthermore, it is clear from Eq. (2) that w_j must obey the condition of detailed balance at equilibrium.

Multiplying Eq. (2) by σ_k and summing over all the $\{\sigma_i\}$ for $i \neq k$, we obtain the equation for the evolution of the order parameter or average spin $q_k(t) = \langle \sigma_k(t) \rangle$:

$$\frac{dq_k(t)}{dt} = -2 \langle \sigma_k(t) w_k(\{\sigma\} \rightarrow \{\sigma'\}, t) \rangle \quad (3)$$

and similarly the time evolution of the pair-correlation function $r_{jk}(t) = \langle \sigma_j(t) \sigma_k(t) \rangle$ is described by (for $j \neq k$)

$$\frac{dr_{jk}(t)}{dt} = -2 \langle \sigma_j(t) \sigma_k(t) [w_j(\{\sigma\} \rightarrow \{\sigma'\}, t) + w_k(\{\sigma\} \rightarrow \{\sigma'\}, t)] \rangle \quad (4)$$

with $j = k$ corresponding to the trivial case $r_{jj}(t) = 1$ for all t .

So far, the above formalism is completely general, i.e., we have made no assumptions about the nature of the local dynamics of the system as expressed in the form of the transition probabilities w_j . Now we start to apply this formalism to our system of two-species n -molecule chemical reactions given by (1): the configuration $\{\sigma_i\}$ of the system at any time t is then a one-dimensional lattice each site i of which is occupied by either an $A(\sigma_i = +1)$ or an $X(\sigma_i = -1)$ particle. The average value of the spin $q(t) = (1/N) \sum_{i=1}^N \langle \sigma_i(t) \rangle$ then corresponds to the difference between the average concentrations of A and X particles $q(t) = C_A(t) - C_X(t)$ on this fully occupied lattice, normalized to $C_A(t) + C_X(t) = 1$.

For the sake of simplicity, we assume both the forward and backward reactions in (1) to occur at a rate of unity. In this paper, we shall explicitly consider the (i) bimolecular ($n = 2$) and (ii) trimolecular ($n = 3$) cases; these are actually the interesting cases for the one-dimensional system $z = 2$, which should cross over to MF behavior at $n = 2$.

2.1. Bimolecular Reaction

This is realized as follows: at each time step, the particle at site i picks with a probability of $1/2$ one of its neighbors j ($j = i + 1$ or $i - 1$) to react with. If this neighbor j is an X particle ($\sigma_j = -1$), then the particle at i changes state $\sigma_i \rightarrow -\sigma_i$. The time evolution of the concentration difference $q(t)$ from simulating this process is shown in Fig. 1 for two different random initial states with concentration $q(0) = 0.5$ and $q(0) = -1$, i.e., one-fourth X particles and all X particles, respectively.

In terms of Eq. (2), this process can be described by the transition probability

$$w_j(\{\sigma\} \rightarrow \{\sigma'\}, t) = \frac{1}{2} - \frac{1}{4}[\sigma_{j-1}(t) + \sigma_{j+1}(t)] \tag{5}$$

Substituting (5) in (3), we obtain for the average concentration difference

$$\frac{dq_k(t)}{dt} = -q_k(t) + \frac{1}{2} [r_{k-1,k}(t) + r_{k,k+1}(t)] \tag{6}$$

As for the average pair correlation $r_{jk}(t) = \langle \sigma_j(t) \sigma_k(t) \rangle$ for $j \neq k$, we get from (4)

$$\frac{dr_{jk}(t)}{dt} = -2r_{jk}(t) + \frac{1}{2} [t_{j-1,j,k}(t) + t_{j,j+1,k}(t) + t_{j,k-1,k}(t) + t_{j,k,k+1}(t)] \tag{7}$$

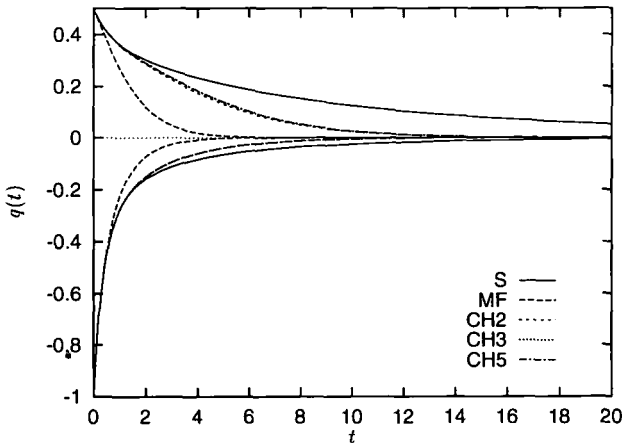


Fig. 1. Evolution of the concentration difference $q(t)$ in the bimolecular system: simulations (S) for $N = 10,000$, mean-field solution (MF), and solutions of coupled hierarchy (CH2, 3, 5) for two different random initial states $q(0) = 0.5$ and $q(0) = -1$.

where now the three-point correlations $t_{ijk}(t) = \langle \sigma_i(t) \sigma_j(t) \sigma_k(t) \rangle$ have entered the picture.

2.2. Trimolecular Reaction

For this case, at each time step, the particle at site i changes state if *both* its neighbors are X particles, i.e., $\sigma_{i\pm 1} = -1$. The time evolution of the concentration difference from simulating this process is shown in Fig. 2 for the same two initial states as in Fig. 1 for the bimolecular process. The transition probability of this reaction can be written

$$w_j(\{\sigma\} \rightarrow \{\sigma'\}, t) = \frac{1}{4}[1 - \sigma_{j-1}(t)][1 - \sigma_{j+1}(t)] \quad (8)$$

Once again, from (8), (3), and (4) we obtain the following two equations for the time evolution of the average concentration difference and the average pair correlation, respectively:

$$\frac{dq_k}{dt} = -\frac{1}{2}q_k(t) + \frac{1}{2}[r_{k-1,k}(t) + r_{k,k+1}(t) - t_{k-1,k,k+1}(t)] \quad (9)$$

$$\begin{aligned} \frac{dr_{jk}(t)}{dt} = & -r_{jk}(t) + \frac{1}{2}[t_{j-1,j,k}(t) + t_{j,j+1,k}(t) + t_{j,k-1,k}(t) + t_{j,k,k+1}(t)] \\ & - \frac{1}{2}[s_{j-1,j,j+1,k}(t) + s_{j,k-1,k,k+1}(t)] \end{aligned} \quad (10)$$

with the four-point correlations s_{ijkl} now entering the picture.

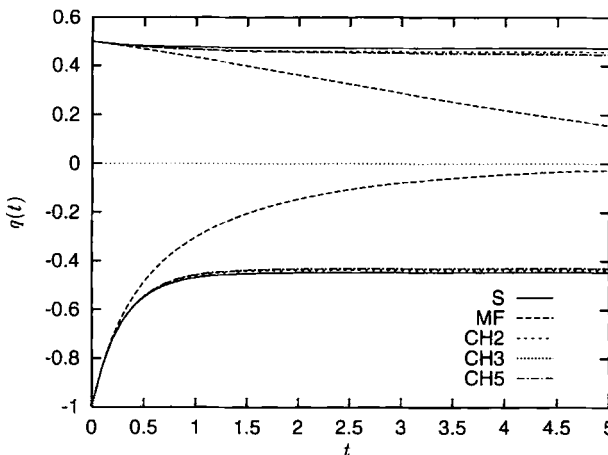


Fig. 2. Evolution of the concentration difference $q(t)$ in the trimolecular system: simulations (S) for $N = 10,000$, mean-field solution (MF), and solutions of coupled hierarchy (CH2, 3, 5) for two different random initial states $q(0) = 0.5$ and $q(0) = -1$.

We note that for both reaction schemes described above, the transition probability at the site i is independent of the state of the particle at that site itself and depends only on those of its nearest neighbors. The former fact is due to the hard-core nature of the underlying microscopic interactions in our model and to the assumption of equal reaction rates for the forward and backward reactions in (1); the latter reflects the essentially short-range nature of the reactive dynamics. In principle, the hard-core assumption can be avoided by realizing the reactions of Eq. (1) differently: several particles can be allowed to coexist at a single site and the reactions carried out on the site. This would result in the transition probability at site j depending on the state of particles at site j . However, such a realization would neglect the role of dimensionality or coordination number, precisely the properties that we are interested in focusing on.

Owing to the above-described structure of the transition probabilities, the dynamical evolution equations (6), (7), (9), and (10) for each subsequent moment of the probability distribution depend on higher moments. This makes the exact solution of the time-evolution equations impossible for these systems, unlike in the Glauber solution for the Ising model,⁽⁵⁾ where the time-dependent behavior was governed by closed equations.

3. THE COUPLED HIERARCHY OF DYNAMICAL EQUATIONS

We now introduce the fluctuation correlation function

$$f_n(t) = \langle \delta\sigma_i(t) \delta\sigma_{i+n}(t) \rangle \quad (11)$$

with $\delta\sigma_i = \sigma_i - \langle \sigma \rangle$ and variance given by

$$f_0(t) = 1 - q^2(t) \quad (12)$$

for all t .

We shall assume translational invariance from here on, implying that the fluctuation correlations depend only on the distance n between the sites in question as in (11), and that $q_k(t) = q(t)$ is independent of position k in the thermodynamic limit $N \rightarrow \infty$. However, before going further, we should briefly mention that the dynamical equations (6) and (9) are extremely rich in structure and can admit wavefront solutions on retention of the spatial or k dependence of $q_k(t)$, an aspect that is being investigated currently in a separate work.

The evolution in time of the nearest neighbor (nn) fluctuation correlations $f_1(t)$ obtained from simulations of the bimolecular and trimolecular processes is shown in Fig. 3 and 4, respectively. These are once again for the two different initially uncorrelated states $q(0) = 0.5$ and $q(0) = -1.0$,

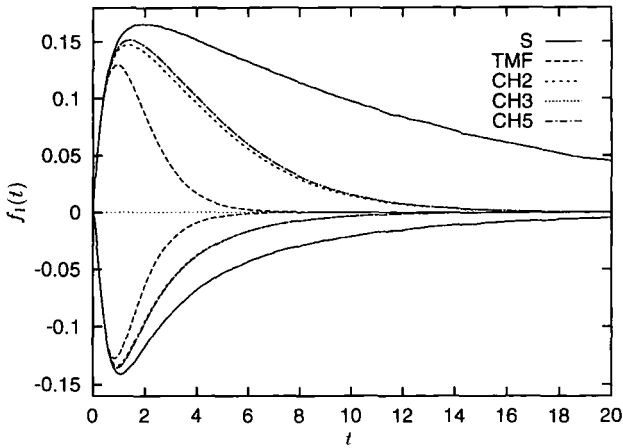


Fig. 3. Evolution of nn fluctuation correlations $f_1(t)$ in the bimolecular system: simulations (S) for $N=10,000$, truncation with MF solution (TMF), and solutions to coupled hierarchy (CH2, 3, 5) for two different random initial states $q(0)=0.5$ (upper curves) and $q(0)=-1$ (lower curves).

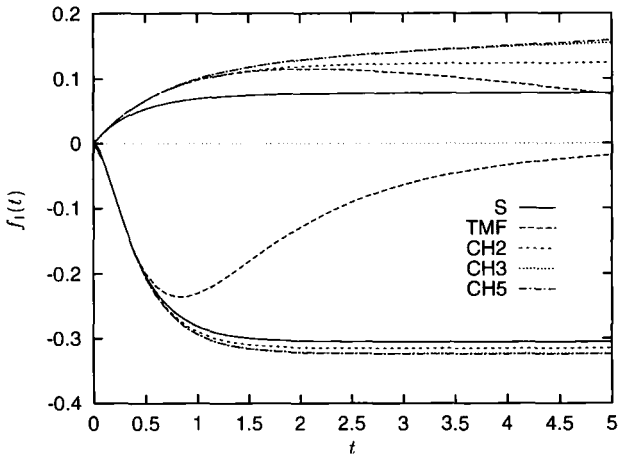


Fig. 4. Evolution of nn fluctuation correlations $f_1(t)$ in the trimolecular system: simulations (S) for $N=10,000$, truncation with MF solution (TMF), and solutions to coupled hierarchy (CH2, 3, 5) for two different random initial states $q(0)=0.5$ (upper curves) and $q(0)=-1$ (lower curves).

both with $f_1(0) = 0$. A comparison of Figs. 2 and 4 with Figs. 1 and 3 shows immediately the intrinsic difference between the bimolecular and trimolecular processes: in the former, the system relaxes to a state of zero concentration difference $q(t)$ between A and X particles and zero fluctuation correlation $f_1(t)$ for any initial state $q(0)$, whereas in the latter, the system shows significant memory effects by freezing into a nonequilibrium state characterized by final $q(t)$ and $f_1(t)$ that depend on the initial state $q(0)$. For both processes, the initial states $q(0) > 0$, characterized by more A than X particles show a positive fluctuation correlation that can be explained as follows: since A clusters can only be eaten up from the boundaries, there is a tendency for clustering, resulting in positive correlations. The initial states $q(0) < 0$, which contain more X particles on the other hand, show negative nn fluctuation correlations, since X clusters can be eaten from the middle, resulting in a tendency toward alternating of the two species.

3.1. Bimolecular Process

Equation (6) can be rewritten in terms of the fluctuation correlations (11) as

$$\frac{dq(t)}{dt} = q(t)[q(t) - 1] + f_1(t) \quad (13)$$

The mean field (MF) equation for $q(t)$ is

$$\frac{dq}{dt} = q(q - 1) \quad (14)$$

which is another way of writing the well-known equation of classical kinetics

$$\frac{dC_A}{dt} = -\frac{dC_X}{dt} = C_X^2 - C_A C_X \quad (15)$$

Equation (14) has the solution

$$q(t) = (1 - e^{-Ct})^{-1} \quad (16)$$

where the constant $e^{-C} = [q(0) - 1]/q(0)$ with $q(0)$ being the concentration difference of the initial state. The MF solution is plotted in Fig. 1 for two different initial states and one can observe that it decays to the steady state much faster than the actual system, which is affected by nonzero

fluctuations at finite times (see Fig. 3), even though the asymptotic state is identical to the mean-field one $q(t \rightarrow \infty) = 0$.

On the other hand, Eq. (7) gives the following coupled set of equations for the $f_n(t)$, after truncation of terms of $O(\delta\sigma^3)$ and higher:

$$\frac{df_1(t)}{dt} = -2f_1(t) + q(t)[1 - q^2(t)] + q(t)f_2(t) \quad (17)$$

and for $n \geq 2$

$$\frac{df_n(t)}{dt} = -2[1 - q(t)]f_n(t) + q(t)[f_{n-1}(t) + f_{n+1}(t)] \quad (18)$$

This effectively infinite sequence of coupled equations can be solved by further truncating the hierarchy beyond some finite value of $n = m$, i.e., setting $f_{m+1}(t) = 0$ and solving the resulting set of $m + 1$ coupled equations numerically. We tried this for various values of m and found no change in the solution for $q(t)$ and $f_1(t)$ on increasing m beyond 3 (see Figs. 1 and 3 for exact form of solutions); we may thus expect the $f_n(t)$ to be short range, an observation that will be verified later in this paper. Moreover, while the curves to which the solutions tend in this limit $m \rightarrow \infty$ are substantially closer to those describing the real system than the MF curves were, they are still quite far from being an exact solution. We attribute this fact to the existence of nonnegligible three-point fluctuations, which were neglected in

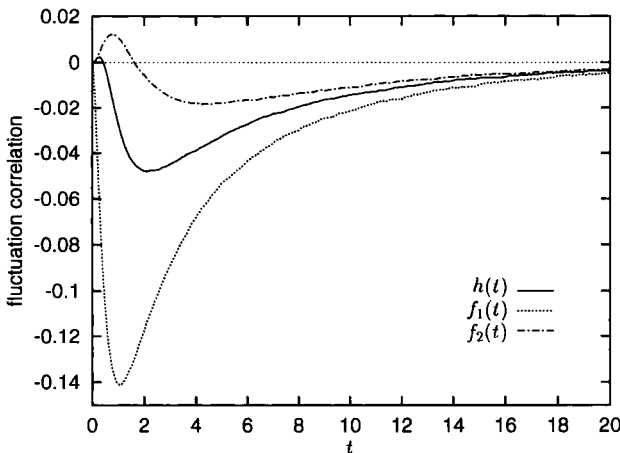


Fig. 5. Comparative evolution in the bimolecular system of the nn pair fluctuation correlation $f_1(t)$, the nnn pair fluctuation correlation $f_2(t)$ and the nn three-point fluctuation correlation $h(t)$, all starting from the random initial state with $q(0) = -1$.

the truncation scheme used to obtain the coupled hierarchy (17)–(18) above. See Fig. 5 for results of the simulation of the evolution of the n three-point fluctuation correlation $h(t) = \langle \delta\sigma_{i-1}(t) \delta\sigma_i(t) \delta\sigma_{i+1}(t) \rangle$ that verify this assertion.

3.2. Trimolecular Process

Similarly, for the trimolecular case, neglecting three-point fluctuations, we can rewrite Eq. (9) as follows:

$$\frac{dq(t)}{dt} = -\frac{1}{2}q(t)[q(t)-1]^2 - [q(t)-1]f_1(t) - \frac{1}{2}q(t)f_2(t) \quad (19)$$

Thus, we have the MF equation for the trimolecular process

$$\frac{dq}{dt} = -\frac{1}{2}q(q-1)^2 \quad (20)$$

which again reduces to classical kinetics, giving

$$\frac{dC_A}{dt} = -\frac{dC_X}{dt} = C_X^3 - C_A C_X^2 \quad (21)$$

The solution to Eq. (20) is plotted in Fig. 2 along with the actual behavior of the system; one sees that neither the asymptotic stable state nor the time evolution of the system follows the MF equations.

For the fluctuation correlations $f_n(t)$, we get from Eq. (10) the following set of coupled equations, again after having truncated terms of $O(\delta\sigma^3)$ and higher:

$$\frac{df_1(t)}{dt} = 2[q^2(t)-1]f_1(t) + q(t)[q(t)+1]f_2(t) + q(t)[q(t)-1][q^2(t)-1] \quad (22)$$

and for $n \geq 2$

$$\frac{df_n(t)}{dt} = -[q(t)-1]^2 - q(t)[q(t)-1][f_{n-1}(t) + f_{n+1}(t)] \quad (23)$$

Once again, as for the bimolecular case, we solve the coupled equations numerically by truncating further at various values of m . We find (see Fig. 4) that already at $m = 2$, there is remarkably good agreement with the simulations, both in terms of the non-MF asymptotic stable state and in

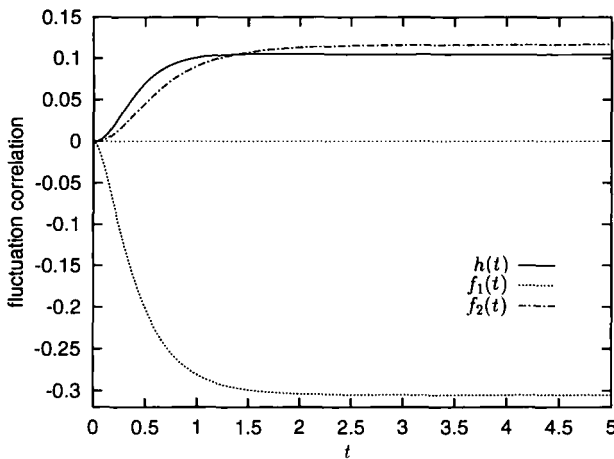


Fig. 6. Comparative evolution in the trimolecular system of the nn pair fluctuation correlation $f_1(t)$, the nnn pair fluctuation correlation $f_2(t)$ and the nn three-point fluctuation correlation $h(t)$, all starting from the random initial state with $q(0) = -1$.

the temporal evolution toward it. In fact, the solution gets somewhat worse by increasing m , perhaps due to the fact that this involves including longer range pair correlations while the whole scheme ignores three-point fluctuation correlations like $h(t) = \langle \delta\sigma_{i-1}(t) \delta\sigma_i(t) \delta\sigma_{i+1}(t) \rangle$, which can be larger than the $f_n(t)$ for large n . It is shown in Fig. 6 that in fact this is already the case at $n = 2$.

3.3. Approximation of Two Coupled Equations

We have found that for both bimolecular and trimolecular processes, increasing the order m of the coupled hierarchy of equations beyond 2 does not improve the ability of the equations to describe the actual behavior of the system (see Figs. 1–4). Thus, we restrict ourselves to $m = 2$ in the following discussion, i.e., to the pair of equations describing the evolution of the average concentration difference $q(t)$ and the nn fluctuation correlation $f_1(t)$, respectively (labeled CH2 in Figs. 1–4), setting $f_n(t) = 0$ for $n \geq 2$.

For the bimolecular process, then, we have the coupled system CH2

$$\frac{dq}{dt} = q(q-1) + f_1 \quad (24)$$

$$\frac{df_1}{dt} = -2f_1 + q(1-q^2) \quad (25)$$

for which the asymptotic steady state ($q(t \rightarrow \infty), f_1(t \rightarrow \infty)$) has only two possible solutions: (0, 0) and (1, 0), the first corresponding to the MF steady state and the second to the trivial special case of a configuration of entirely A particles where nothing evolves. For a rough idea about the long-time relaxation of the fluctuation correlation $f_1(t)$, we substitute the MF solution (16) into Eq. (25) for $f_1(t)$; the resulting equation is easily solved to give

$$f_1(t) = \left(\frac{q}{q-1} \right)^2 \left(-\frac{1}{2}q^2 + q + \ln q + \frac{1}{q} + k \right) \quad (26)$$

where the long-time limit $t \rightarrow \infty, q \rightarrow 0$ gives $f_1 \rightarrow q(1 + 2q)$. Thus, we have

$$f_1(t \rightarrow \infty) \rightarrow q(t) \quad (27)$$

From (16), $q(t \rightarrow \infty) \rightarrow -e^{-(t-C)}$ and therefore we expect to see exponential relaxation for both the average concentration difference and the fluctuation correlation as will be verified in Section 5. The approximate solution (26) is also plotted in Fig. 3 and labeled TMF for "truncated with mean field".

For the trimolecular process, on the other hand, we have the coupled system CH2 given by

$$\frac{dq}{dt} = -\frac{1}{2}q(q-1)^2 - (q-1)f_1 \quad (28)$$

$$\frac{df_1}{dt} = (q^2 - 1)[2f_1 + q(q-1)] \quad (29)$$

which has three possible steady-state solutions: (0, 0), (1, f_1) and ($q, -\frac{1}{2}q(q-1)$); the first two are, as mentioned before, for the bimolecular case, but now we also have the nonequilibrium state characterized by the nonzero nn fluctuation correlation

$$f_1(t \rightarrow \infty) = -\frac{1}{2}q(t)[q(t) - 1] \quad (30)$$

As can be observed in Fig. 4 by comparing the solution for $m = 2$ with the simulations, this value is very close to the one attained by the actual system at the steady state. Also, see Table I for a comparison of values of f_1 at the steady state obtained from various analytical methods described in this paper with the value obtained from simulations. Once again, in Fig. 4, the curve labeled TMF corresponds to the solution obtained by substituting the MF solution for $q(t)$ into Eq. (29) for $f_1(t)$.

Table I. Values of Average Concentration Difference $q(\infty)$ and Average nn Fluctuation Correlation $f_1(\infty)$ at the Steady State from Simulation (SIM), Coupled Hierarchy of Two Equations [CH2, Eqs. (28) and (29)], and the g-Approximation [g-app, Eq. (48)] for the Trimolecular System

$q(0)$	$q(\infty)$		$f_1(\infty)$		
	SIM	CH2	SIM	CH2	g-app
-1.0	-0.447	-0.4385	-0.306	-0.315	-0.306
-0.5	-0.3261	-0.321	-0.204	-0.212	-0.210
-0.25	-0.186	-0.182	-0.101	-0.107	-0.109
0.25	0.223	0.216	0.067	0.085	0.085
0.5	0.474	0.458	0.080	0.124	0.117

Thus, the memory effects present in the trimolecular process can already be seen from this simple model of two coupled equations, which predicts quite accurately the relation between the fluctuation correlations and the average concentration in the frozen asymptotic state.

4. EXTENDED BETHE-TYPE ANSATZ

There are other ways of improving on the mean-field analysis that are not based on the type of truncations introduced in the previous section; in this section we discuss one such alternative method and show its comparative success for the bimolecular case. This method is also a hierarchical one: the zeroth order of the hierarchy is, as before, the MF solution; the first step is a Bethe-type ansatz. In the MF analysis, we focus on a single particle, replacing all the other particles by a single “mean field” in terms of their effect on the chosen particle and then solving for the time evolution of the average state of the particle. The Bethe-type ansatz (BA) goes a step further in focusing on two particles, and again replacing the rest by a mean field, thus retaining the correlation between the two chosen particles. Here we extend the Bethe-type ansatz to the case of $n > 2$ particles and show that the solution converges to the one describing the behavior of the full bimolecular process.

For our bimolecular model, then, at the master equation level, the MF gives (focusing on the state σ_j of the particle j , replacing the rest of the particles by the average state $\langle \sigma \rangle$) and abbreviating $w_j(\{\sigma\} \rightarrow \{\sigma'\}, t)$ by w_j , we have

$$w_j = \frac{1}{2}(1 - \langle \sigma \rangle) \quad (31)$$

and we thus once again obtain the MF solution Eq. (14), with $q = \langle \sigma_j \rangle$, the average concentration difference. Now, for the Bethe-type ansatz, we retain σ_j and σ_{j+1} and average over the rest of the spins, thus

$$w_j = \frac{1}{2} - \frac{1}{4}(\langle \sigma \rangle + \sigma_{j+1}) \tag{32}$$

$$w_{j+1} = \frac{1}{2} - \frac{1}{4}(\langle \sigma \rangle + \sigma_j) \tag{33}$$

which when substituted in (3) and (4) give respectively for the average concentration difference $q(t)$ and the average nn fluctuation correlation $f_1(t) = \langle \delta \sigma_j \delta \sigma_{j+1} \rangle$

$$\frac{dq}{dt} = q(q-1) + \frac{1}{2}f_1 \tag{34}$$

$$\frac{df_1}{dt} = -2f_1 + q(1-q^2) \tag{35}$$

The solutions to this coupled system are plotted in Figs. 7 and 8, along with the actual behavior.

But now we can extend the Bethe-type ansatz to n consecutive particles, thus creating a new hierarchical scheme of equations. The primary step in this extension is the $n=3$ case: we retain the particles at $j-1$, j , and $j+1$ and all correlations between them, while replacing everything else by the mean field. In addition to the quantities $q(t)$ and $f_1(t)$ as before,

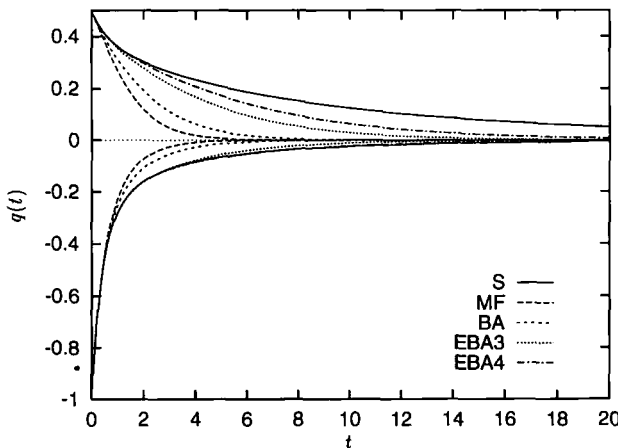


Fig. 7. Evolution of the average concentration difference $q(t)$ in the bimolecular system using Bethe-type ansatz (BA) and extended Bethe-type ansatz (EBA3, 4) for two different random initial states $q(0) = 0.5$ and $q(0) = -1$.

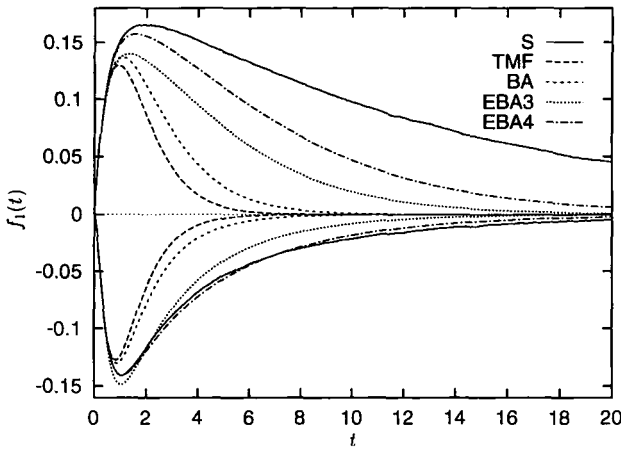


Fig. 8. Evolution of the average nn fluctuation correlation $f_1(t)$ in the bimolecular system using Bethe-type ansatz (BA) and extended Bethe-type ansatz (EBA3,4) for two different random initial states $q(0) = 0.5$ and $q(0) = -1$.

we now have the next nearest neighbor (nnn) pair correlation $r_2(t) = \langle \sigma_{j-1} \sigma_{j+1} \rangle$ and the three-point correlation $t_1(t) = \langle \sigma_{j-1} \sigma_j \sigma_{j+1} \rangle$ that obey the coupled system of four equations

$$\begin{aligned}
 \frac{dq}{dt} &= q(q-1) + f_1 \\
 \frac{df_1}{dt} &= -2f_1 + q - \frac{3}{2}q^3 - \frac{3}{2}qf_1 + \frac{1}{2}t_1 \\
 \frac{dr_2}{dt} &= -2r_2 + t_1 + qr_2 \\
 \frac{dt_1}{dt} &= -3t_1 + q^2 + f_1 + r_2 + qt_1
 \end{aligned} \tag{36}$$

Continuing this process to $n=4$ particles, we obtain a coupled set of seven equations and so on. The solutions to this extended Bethe-type ansatz are obtained by solving the coupled equations numerically and are plotted in Figs. 7 and 8 for $q(t)$ and $f_1(t)$ respectively. They converge monotonically towards the actual behaviour as n is increased, and one can see that already at $n=4$, the agreement is very good for the system with the initial state given by $q(0) = -1$, i.e. all X particles, whereas for systems with a large number of A particles, the convergence is somewhat slower, but still quite evidently toward the actual behavior.

We attribute the comparatively better convergence of this method to the essentially short-range nature of correlations in the system. A hierarchical method in which one improves the approximation by including longer range pair-correlations while neglecting from the beginning higher order short-range correlations, as was done in Section 3, would have poor convergence properties for such systems. Our extended Bethe-type ansatz, however, improves the approximation by including more spins while retaining all orders of correlations between them, which are not negligible for such systems in comparison with pair correlations [see Figs. 7 and 8 for the simultaneous evolution of $f_1(t)$, $f_2(t)$, and $\langle \delta\sigma_{i-1}\delta\sigma_i\delta\sigma_{i+1} \rangle$].

5. RELAXATION TO THE STEADY STATE AND PATTERN ENTROPY

In Section 3, we made some qualitative observations regarding the relaxation of the average concentration difference $q(t)$ and of the nn fluctuation correlation $f_1(t)$ toward the steady state in connection with Figs. 1–4. In this section, we shall have a more detailed look at the long-time relaxation behavior of the two processes.

Figures 9 and 10 describe the relaxation behavior $q(t \rightarrow \infty)$ and $f_1(t \rightarrow \infty)$ for the bimolecular process (for Figs. 9–12, the labels for the various curves within a figure are arranged starting from the top to the bottom according to the way they are ordered on the right hand extreme of the figure). One can see that the long-time behavior is exponential. Furthermore, by superposing Fig. 9 on Fig. 10, one verifies that Eq. (27) is exactly true at long times; thus $q(t \rightarrow \infty) \simeq f_1(t \rightarrow \infty) \simeq e^{-\beta t}$. When the initial state contains more X particles, the coefficient β is apparently independent of the initial state, i.e., for $q(0) = C_A(0) - C_X(0) < 0$, we have $\beta \simeq 0.14$; however, when there are more A particles in the initial state, the relaxation rate is much slower and depends on the initial concentration, going to zero when there are only A particles in the system. This slower relaxation is due to the fact that reactions can take place only at the boundary of A clusters, and we find a kind of crossover in this relaxation behavior when we go from X -dominated configurations to A -dominated ones. In comparison, the MF solution (14) corresponds to a much faster decay rate of $\beta = 1$, independent of the initial state.

For the trimolecular system, on the other hand (see Figs. 11 and 12), the approach to the steady state appears to be exponential, even at shorter times, i.e., $q(t) = q(\infty) + [q(0) - q(\infty)] e^{-\alpha t}$ and $f_1(t) = f_1(\infty)(1 - e^{-\alpha t})$, with α varying continuously from about 2 for an initial state $q(0) = 0.5$, i.e., 75% A particles, to about 2.9 for $q(0) = -1$, i.e., all X particles. Thus, the trimolecular system freezes into its nonequilibrium steady state a good

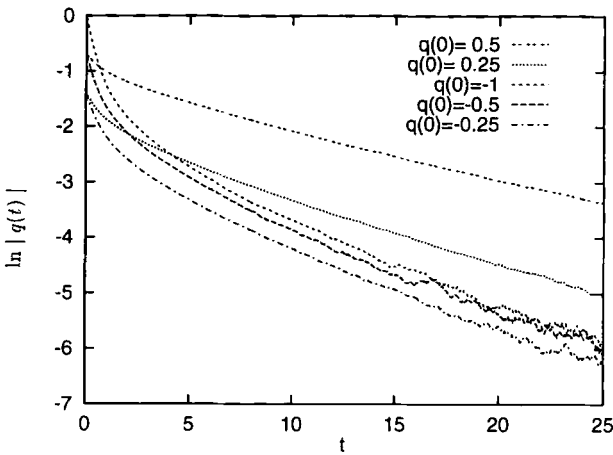


Fig. 9. Semilog plot of $|q(t)|$ vs. t for the bimolecular system from simulations for various random initial states.

order of magnitude faster than the bimolecular one relaxes to its equilibrium state, as can also be inferred from a comparison of Figs. 1 and 2 with Figs. 3 and 4.

Next, we look at the time evolution of pattern entropies associated with the distribution of the sizes of domains of the two species of particles:

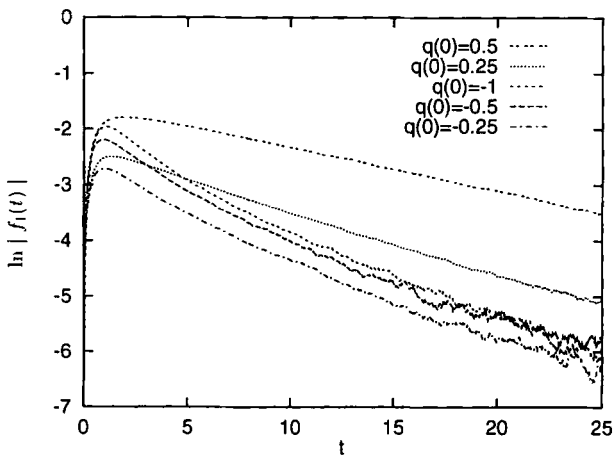


Fig. 10. Semilog plot of $|f_1(t)|$ vs. t for the bimolecular system from simulations for various random initial states.

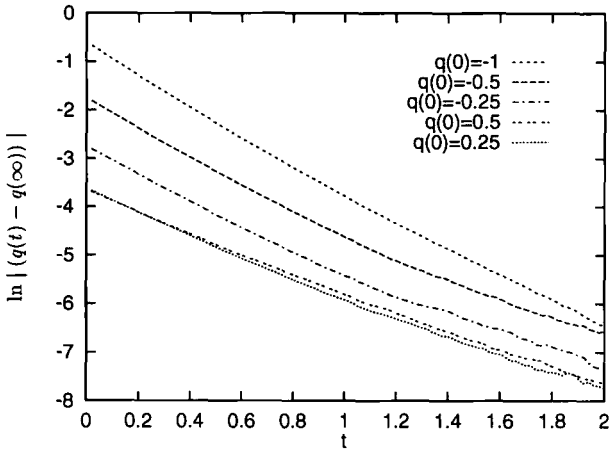


Fig. 11. Semilog plot of $|q(t) - q(\infty)|$ vs. t for the trimolecular system from simulations for various random initial states.

the static entropy, a measure of the static complexity of the pattern, has been defined⁽⁸⁾ as

$$S_p = -\sum_j Q(j) \ln Q(j) \tag{37}$$

where $Q(j)$ is the probability that a lattice point belongs to a domain of

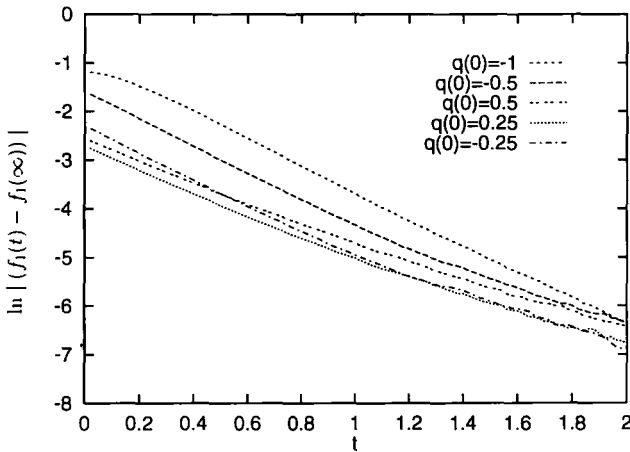


Fig. 12. Semilog plot of $|f_1(t) - f_1(\infty)|$ vs. t for the trimolecular system from simulations for various random initial states.

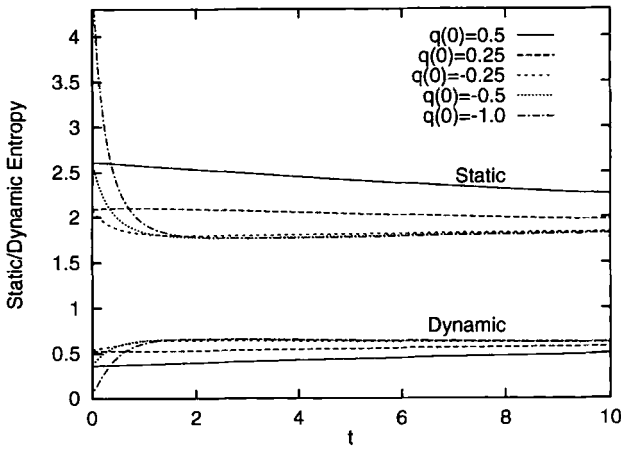


Fig. 13. Evolution of static and dynamic pattern entropies in the bimolecular system for various random initial states.

size j . To study the pattern dynamics, we need in addition to look at the pattern dynamical entropy given by

$$S_d = - \sum_{j,k} Q(j) T(j \rightarrow k) \ln T(j \rightarrow k) \tag{38}$$

where $T(j \rightarrow k)$ is the probability that a lattice point makes the transition from a domain of size j to one of size k . The evolution of S_p and S_d with

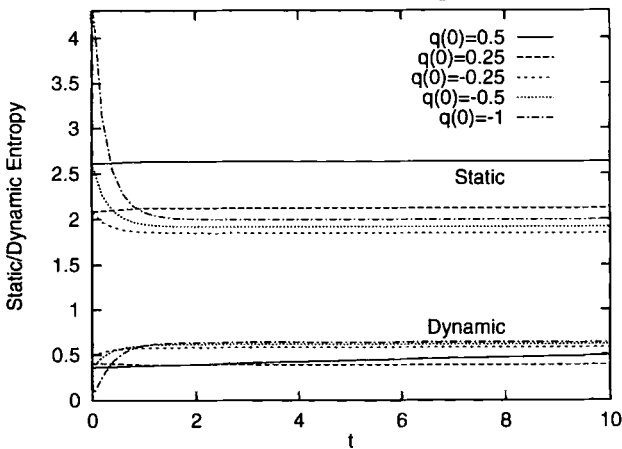


Fig. 14. Evolution of static and dynamic pattern entropies in the trimolecular system for various random initial states.

time for bimolecular and trimolecular processes are shown in Figs. 13 and 14, respectively, for a variety of different random initial states. In particular, the initial state $q(0) = -1$ corresponding to all X particles must have zero initial static entropy; however, after any finite time step, it attains a very high entropy: thus the curves for this initial state appear to originate from a point of very high static entropy.

For the bimolecular process, the static entropies for all the initial states approach the same value asymptotically: the value associated with a random configuration of an equal number of A and X particles. The asymptotic dynamic entropy is also independent of the initial state, once again showing the nonexistence of memory effects for the bimolecular system. However, as was observed in the relaxation of $q(t)$ and $f_1(t)$, the approach to the asymptotic value appears to be the same for all $q(0) < 0$, i.e., all initial configurations having more X than A particles. For configurations having more A particles initially, i.e., $q(0) > 0$, the approach is much slower (see Fig. 13).

For the trimolecular system (see Fig. 14), we see memory effects in the entropies of the asymptotic state that mirror the memory effects found in the asymptotic behavior of $q(t)$ and $f_1(t)$. The static entropy attains its asymptotic value within a couple of time steps; however this asymptotic value varies continuously with the composition of the initial state, with the state $q(0) = 0.5$ that contains the maximal concentration of A particles having maximum spatial complexity and maximum temporal freezing (as expected, due to frozen A clusters) characterized by high S_p and low S_d .

6. SPATIAL ORGANIZATION IN STEADY STATE

We have seen that the bimolecular system is characterized at the steady state by zero correlation fluctuation f_n for all n , while the trimolecular system is characterized by nonzero fluctuation correlations. In this section, we will study the spatial decay of the fluctuation correlations in the steady state, i.e., the dependence of $f_n(t \rightarrow \infty)$ on n for the trimolecular system.

Equation (9) gives at the steady state

$$q = r_{k-1,k} + r_{k,k+1} - t_{k-1,k,k+1} \tag{39}$$

Similarly, (10) gives

$$[2r_{jk} = t_{j-1,j,k} + t_{j,j+1,k} + t_{j,k-1,k} + t_{j,k,k+1} - s_{j-1,j,j+1,k} - s_{j,k-1,k,k+1}] \tag{40}$$

To obtain any further information about the spatial dependence of the two-point correlations f_n at the steady state, we must first make some

approximations for the higher point correlations in (39) and (40). The zeroth-order (MF) approximation simply neglects correlations altogether and gives for the conditional average

$$\langle \sigma_l | \sigma_k \rangle = \sum_{\sigma_l} \sigma_l P(\sigma_k, \sigma_l) = \langle \sigma \rangle P(\sigma_k) \quad (41)$$

implying a completely uncorrelated probability distribution $P(\sigma_k, \sigma_l) = P(\sigma_k) P(\sigma_l)$. We now invoke the linearization about this zeroth order or MF expression, namely the “g-approximation”,⁽⁹⁾ which improves on (41) as follows

$$\langle \sigma_l | \sigma_k \rangle = [\langle \sigma \rangle + g(k, l)(\sigma_k - \langle \sigma \rangle)] P(\sigma_k) \quad (42)$$

with $g(k, l) = \langle \delta \sigma_k \delta \sigma_l \rangle / \langle \delta \sigma^2 \rangle$. The g-approximation (42) has been found to be a very useful technique in previous work on the master-equation description of reaction-diffusion systems.⁽¹⁰⁾ It is exact for Gaussian distributions. From (42), we can write for the correlations

$$r_{kl} = q^2 + g(n) \langle \delta \sigma^2 \rangle \quad (43)$$

where $g(n) = g(k, l)$ for $n = |k - l|$, assuming as before that the correlations depend only on the distance between the sites. To break down higher point correlations, like $t_{k-1, k, k+1} = \langle \sigma_{k-1} \sigma_k \sigma_{k+1} \rangle$ in (39) and (40) in a similar manner, we write for $l > k$

$$P(\sigma_{k-1}, \sigma_k, \sigma_l) = P(\sigma_{k-1}, \sigma_k) P_c(\sigma_l | \sigma_k) \quad (44)$$

where we have made the assumption of spatial Markovianity, i.e., we have assumed that the conditional probability P_c for σ_l depends only on the value σ_k in the nearest cell and not on that in other cells further away. We are then in a position, using Eqs. (43) and (44), to write the three-point and higher correlations appearing in (40) as follows for $l > k$:

$$\begin{aligned} t_{k, k+1, l} &= t_{k, l-1, l} \\ &= q^3 + q(1 - q^2)[g(1) + g(n-1) - g(1)g(n-1)] \end{aligned} \quad (45)$$

$$\begin{aligned} t_{k-1, k, l} &= t_{k, l, l+1} \\ &= q^3 + q(1 - q^2)[g(1) + g(n) - g(1)g(n)] \end{aligned} \quad (46)$$

$$\begin{aligned} s_{k-1, k, k+1, l} &= s_{k, l-1, l, l+1} \\ &= q^4 + 2(q^2 - q^4)g(1) + (q^2 - q^4)g(n-1) \\ &\quad + (2q^4 - 3q^2 + 1)g(1)g(n-1) - (q^2 - q^4)g(1)^2 \\ &\quad + (q^2 - q^4)g(1)^2g(n-1) \end{aligned} \quad (47)$$

Substituting (43) and (45) in (39), we get the following solution for $g(1) = f_1/(1 - q^2)$:

$$g(1) = \frac{1}{q} \left[q - 1 + \left(\frac{1 - q}{1 + q} \right)^{1/2} \right] \tag{48}$$

As it turns out, this expression predicts quite accurately the value of the nn fluctuation correlation in the steady state (see Table I for a comparison of the values obtained for f_1 in the steady state from the different methods with the actual values from simulations).

Having thus evaluated f_1 , we can go further and look at the spatial (i.e., n) dependence of f_n in the steady state. Specifically, substituting Eqs. (43) and (45)–(48) into (40), we obtain the following recursive relation:

$$\frac{g(n)}{g(n - 1)} = F(q) \tag{49}$$

with

$$F(q) = \frac{1}{q} \left\{ q + 1 - 2[(1 - q)(1 + q)]^{1/2} + \left(\frac{1 - q}{1 + q} \right)^{1/2} \right\} \tag{50}$$

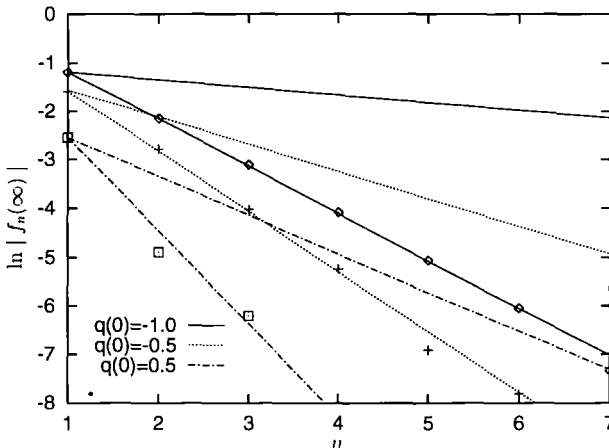


Fig. 15. Spatial decay of fluctuation correlations $f_n(\infty)$ at the steady state for three different initial states of the trimolecular system. Lines without points indicate results from the g -approximation, corresponding lines with points indicate the values from simulations for the same initial state $q(0)$.

The fact that the ratio in Eq. (49) is independent of n shows that the $g(n)$ and therefore the fluctuation correlations f_n decay exponentially with n and are therefore short ranged. This is borne out by simulations (see Fig. 15); however, the coefficient $F(q)$ predicted in (50) as characterizing this exponential decay is found to consistently describe a slower decay than the one actually observed.

7. DISCUSSION

We have devised and illustrated here various methods for effectively probing the temporal evolution of the average concentration and fluctuation correlations in reactive systems of low spatial dimension. The formalism developed here is easily generalizable and applicable to the study of the dynamics of any lattice model of reactive species in any dimension. There is nothing in the structure of the transition probabilities (5) and (8) that makes the formalism more appropriate for these cases. The resulting equations for the average concentration and the fluctuation correlations obtained by inserting the relevant transition probabilities in (3) and (4) can be subsequently studied using the various methods described here. We have explicitly implemented these methods for the n -molecule reaction of Eq. (1) for the specific cases of interest $n=2$ and $n=3$ (there is known to be a crossover to a mean-field equilibrium steady state between these two values, as discussed in Section 1) and shown their comparative success and limitations. We started with a master equation description of the dynamics based on a lattice model of the Glauber type. The dynamical equations were obtained from the master equation first by neglecting terms of order higher than 2 in the fluctuations. The hierarchy of equations obtained in this way for the pair correlations $f_n(t)$ between sites at a distance n from each other does not (in the limit $n \rightarrow \infty$) converge to the real behavior of the system, as is verified by simulations. This is shown to be due to the existence of substantial three-point fluctuation correlations in both systems. However, the pair of coupled equations CH2 for the average concentration difference between the species $q(t)$ and the nn fluctuation correlation $f_n(t)$ obtained by truncating the hierarchy at $n=2$ already describe quite well many properties of the systems, such as their long-time relaxation and the values of the average concentration difference and fluctuation correlations at the steady state.

To tackle the problem of nonconvergence of the hierarchy of dynamical equations to the real behavior, we introduced the extended Bethe-type ansatz and demonstrated its comparative success for describing such systems where higher point fluctuation correlations are of a magnitude comparable to the two-point ones, owing to the short-range nature of the

latter. The sets of coupled dynamical equations obtained from this approach are shown to converge to the actual behavior of the full system as the number of particles considered in the ansatz is increased.

We also probed further the relaxation behavior of both systems by detailed simulations that verify long-time exponential relaxation for both systems considered and also simulated the evolution of pattern entropies to show the dynamics of spatial organization.

Finally, we had a closer look at the correlations in the steady state of the trimolecular system (the bimolecular system has zero correlations at the steady state) and calculated analytically the values of the fluctuation correlations at this steady state and found very good agreement with simulational results. Our calculations also predict the exponential decay of spatial correlations at the steady state, as is verified by simulations.

We considered in this work only the case of a one-dimensional lattice, i.e., of coordination number $z=2$, for which the crossover to equilibrium behavior occurs at $n=2$. We believe, however, that the phenomenon is quite general and many results obtained here will apply also to lattices of a different coordination number z with the crossover occurring at a different value of n , but with systems below and above this crossover preserving respectively the properties demonstrated here for $n=2$ and $n=3$ for the case $z=2$. Moreover, we believe that the formalism used in this work can be extended to deal with open systems that continuously exchange particles with their surroundings. In particular, we are interested in dealing with the Schlögl models, which contain the additional step $X \rightleftharpoons B$ after the bimolecular/trimolecular reaction step discussed here.

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