# Intrinsic-noise-induced transitions in chaotic systems

J. Güémez
*Departamento de Física Aplicada, Universidad de Cantabria, E-39005 Santander, Spain*

M.A. Matías
*Departamento de Química Física, Universidad de Salamanca, E-37008 Salamanca, Spain*
(Received 17 June 1994)

The aim of this work is to study the effect of intrinsic or thermodynamic fluctuations on spatially homogeneous systems of coupled chemical reactions exhibiting deterministic chaos. These fluctuations are taken into account by using a mesoscopic representation of the system in which the corresponding master equation is simulated through a Monte Carlo algorithm. The two models of chemical chaos studied in this work exhibit intrinsic-noise-induced transitions, one to a fixed point and the other to infinity. These examples illustrate the kind of dramatic effects that this type of noise may induce if the size of the system is small or moderate. It is shown that the effects of molecular fluctuations are qualitatively similar to the effect of external multiplicative noise, scaling as the square root of the number of particles. It is shown that it is possible to devise a simple model that captures the essence of the noise-induced transitions.

PACS number(s): 05.40.+j, 05.45.+b, 82.40.Bj

## I. INTRODUCTION

In the recent years the study of systems with nonlinear evolution laws has afforded a new source of randomness in nature, namely the concept of deterministic chaos [1], which is completely independent of other sources of external noise introduced by the accuracy of the laboratory equipment, the interaction with the outer world, etc. Low-dimensional deterministic chaos has been proved to be present in a manifold of different experimental situations [2]. The study of chaotic systems is normally carried out by using a mean-field description in terms of a set of macroscopic variables that hopefully capture the system dynamics. In the case of chemical chaos [3] considered here, of which the best known example is the Belousov-Zhabotinsky reaction, the mean-field continuous description can be obtained in a straightforward way from the chemical mechanism through the mass-action law for the reaction rate that describes the chemical reaction in terms of the continuous macroscopic concentrations of the relevant chemical species.

However, this kind of description is only an approximate representation of reality and one would like to be able to have a more fundamental picture of the system. The most fundamental description would be obtained by going down to the level of atoms and molecules and ultimately representing the macroscopic behavior of the system in terms of the laws of quantum mechanics. By using a more realistic point of view, one could try to obtain the macroscopic oscillations by using classical molecular dynamics techniques through the detailed study of the collisions among the relevant atoms or molecules. However, in practice these calculations are quite cumbersome [4], although one can resort to approximate procedures such as Bird's algorithm [5]. The problem is that the subpicosecond time scale typical of molecular events and the typical time scale of chemical oscillations (roughly on the order of some minutes) differ by almost 15 orders of magnitude. Thus, here we shall adopt a mesoscopic representation, which amounts to a coarse-graining procedure in which one takes care of the actual occurrence of the reactive events, skipping much of the detailed information about the collisions. This procedure is intermediate between the microscopic fundamental representation and the macroscopic representation in terms of continuous variables, and is based on the resolution of the so-called master equation [6,7]. This representation ensures that the macroscopic laws are obeyed in the average, but the possibility of fluctuations and correlations between the constituent particles is introduced.

The master-equation representation has firm foundations in the case of chemical reactive collisions, offering a meaningful link between the microscopic collisional reactive events and the macroscopic mass-action law description through kinetic theory arguments [8]. The chemical master equation describes chemical reactions as jump Markov (or memoryless) processes in the discrete space of the populations of every participating chemical species. This equation is a fully legitimate representation of homogeneous (well-stirred) systems if every reactive collision is followed by many nonreactive collisions that allow the system to reestablish the local equilibrium. In practice, solving the master equation by analytical methods is a very difficult task (only possible for a small number of systems). For this reason, in this work we shall resort to stochastic simulations by using a Monte Carlo algorithm put forward by Gillespie [9], to be described later.

Another alternative method that introduces a mesoscopic description for these systems is a reactive lattice-gas cellular automaton [10], as in the work of Wu and Kapral [11,12]. In this approach the system is represented through a lattice with a certain symmetry that

 

may contain a maximum number of particles at each point. The automaton is defined through the rules that update the number of particles at each time. It can be shown [11,12] that each node follows the same time evolution as the corresponding chemical master equation. Thus the results of the automaton simulations are essentially analogous to those presented here. The main advantage of the automaton representation is that the study of spatially inhomogeneous systems is straightforward, making possible the study of systems exhibiting spatiotemporal chaos, patterns, etc. Moreover, the automaton performs only Boolean and integer operations, and, thus, no rounding errors are introduced.

The aim of this work is to consider the effects that these intrinsic or internal fluctuations (or noise) may have on homogeneous (well-stirred) systems in which the strange attractor coexists with other types of attractors. One can expect that the presence of noise in the variables entering the deterministic description will have an important role for the case of chaotic systems, which exhibit sensitive dependence on the initial conditions [1]. Fox and Keizer [13,14] have studied these issues, showing, through the use of a nonlinear Fokker-Planck representation, that the growth of intrinsic fluctuations is governed by the Jacobi matrix, which also determines the Lyapunov exponents. This implies that after some time fluctuations grow to macroscopic size, becoming important compared to the values predicted by the deterministic equations themselves. Moreover, Bracikowski *et al.* [15] have shown for a chaotic multimode laser system that the effect of intrinsic noise for specific trajectories is consistent with the theoretical predictions of Fox *et al.*

A different view on this problem is the one held by Nicolis and Balakrishnan [16], saying in essence that, although the effect of intrinsic fluctuations on the exponential divergence for specific trajectories is beyond question, these trajectories will remain bounded in the basin of attraction of the strange attractor. Being more precise, one needs to look at the change in the invariant distribution, and the corresponding invariant measure, induced by the presence of intrinsic fluctuations. The numerical study of some systems has confirmed [11,12,17,18] that this is the case, and that the usual phenomenological equations in terms of macroscopic variables would retain their usefulness. Moreover, one can devise a Langevin-type treatment [18], with a rapidly fluctuating term representing the intrinsic noise, that exhibits analogous behavior to that of the simulations.

More important appears to be the effect of noise on systems that are not far from the onset of chaos. Wu and Kapral [11,12] have shown that, if the system under study is in a given periodic orbit, then, when intrinsic noise is present, this orbit will be destabilized and the system will explore the corresponding unstable manifold, which spans the strange attractor. These conclusions, also confirmed for other systems [18], are analogous to the well-known effects of external noise on this type of system [19].

However, the aim of the present work is to show that in the case of systems that contain multiple attractors the effect of intrinsic fluctuations is to induce a transition from the strange attractor onto one of the possible competing attractors on a time scale that depends on the size of the system: the larger the system the longer will be the mean time for the transition, although this will always take place if one waits long enough. Thus, in this case the effect of the inclusion of intrinsic noise effects will be to change the invariant distribution from that typical of the strange attractor to that centered around the competing attractor: a fixed point or an attractor at infinity in the examples considered in this work.

In summary, the main conclusion stemming from these studies is that either one has results in agreement with Nicolis and Balakrishnan's predictions [16], in the case that the strange attractor does not have other competing attractors, although this case is not analyzed in this work, or then the invariant distribution is strongly affected by intrinsic fluctuations in the case that multiple attractors coexist, making the macroscopic representation unreliable as advocated by Fox *et al.* However, it will be shown again that a Langevin-type of treatment is able to yield results in agreement with the simulations. It is to be noticed that the possibility of an intrinsic-noise-induced transition was already reported in [11,12,20].

The plan of this article is as follows. In Sec. II Gillespie's method is summarized. Section III considers the Willamowski-Rössler model [21], which offers an example of a noise-induced transition from a strange attractor to a fixed or equilibrium point. Sec. IV deals with a model [22] that is a chemical version of Rössler's model of spiral chaos [23], and that offers an example of a noise-induced transition from a strange attractor to an attractor at infinity (an explosion). Section V considers two simple maps that model the behaviors encountered in the previous two sections. The article closes with the main conclusions from the present work (Sec. VI).

## II. A SURVEY OF GILLESPIE'S METHOD

The aim of this section is to present a self-contained, although greatly simplified, account of the chemical master-equation representation of chemically reactive events and its simulation through the stochastic method introduced by Gillespie [9]. The chemical master equation is a time evolution equation for the conditional probability $P(\mathbf{n},t|\mathbf{n}_0,t_0)$ that if the population of the chemical species, written as a vector $\mathbf{n}\equiv(n_1,\ldots,n_N)$, is $\mathbf{n}_0$ at time $t_0$ then it will be $\mathbf{n}$ at time $t$. This master equation for the temporally homogeneous jump Markov process in the discrete space of the non-negative integer populations of the chemical species can be written in the form [8] (see also [24])

$$\frac{\partial}{\partial t}P(\mathbf{n},t|\mathbf{n}_0,t_0)=\sum_{\mu=1}^{M}\Big[c_\mu h_\mu(\mathbf{n}-\nu_\mu)P(\mathbf{n}-\nu_\mu,t|\mathbf{n}_0,t_0) - c_\mu h_\mu(\mathbf{n})P(\mathbf{n},t|\mathbf{n}_0,t_0)\Big]\,. \tag{1}$$

The chemical master equation (1) describes a system with a series of reaction channels $R_\mu$ $(\mu=1,\ldots,M)$ for

the existing species $S_i$ with stoichiometric coefficients $\nu_i$ having the form

$$\nu_i S_i + \nu_j S_j + \cdots \xrightarrow{k_\mu} \nu_k S_k + \nu_l S_l + \cdots \tag{2}$$

and where for each channel the $t$-independent scalar $c_\mu$ is such that $c_\mu dt$ is the probability that a randomly selected combination of $R_\mu$ reactant molecules at time $t$ will react in the interval $[t, t+dt]$.

The relationship between $c_\mu$, depending on the populations (number of particles) $\mathbf{n}$, and the macroscopic rate constants $k_\mu$, written in terms of the chemical concentrations $\mathbf{x} = \mathbf{n}/V$, can be shown to be [9]

$$c_\mu = k_\mu V^{1-\alpha_\mu} , \tag{3}$$

which essentially guarantees that size extensivity is preserved, as the $\mathbf{n}$ are extensive variables while the $\mathbf{x}$ are intensive. Here $\alpha_\mu$ is the order of reaction $R_\mu$, i.e., $\alpha_\mu = \sum \nu_i$, this sum being extended only to the reagents appearing in reaction $R_\mu$ and $V$ being the volume of the system. In the limit $V \to \infty$ the master equation should become identical to the deterministic representation, as fluctuations become negligible.

The function $h_\mu(\mathbf{n})$ represents the number of distinct combinations of the reactant molecules in the $R_\mu$ reaction, $\mathbf{n} = (n_1, n_2, \ldots)$ being the population vector for every species,

$$h_\mu(\mathbf{n}) = \frac{n_i!}{(n_i - \nu_i)!} \times \frac{n_j!}{(n_j - \nu_j)!} \times \cdots , \tag{4}$$

where the product is extended to all reagents in reaction $R_\mu$ and $n_i$ is the number of molecules of the species $S_i$ with stoichiometric coefficient $\nu_i$. Thus the rate of reaction $R_\mu$ is $a_\mu = c_\mu\, h_\mu(\mathbf{n})$, the total rate being written in the form

$$a(\mathbf{n}) = \sum_{i=1}^{M} c_i h_i(\mathbf{n}) . \tag{5}$$

The key quantity in the practical implementation of the stochastic simulation of the chemical master equation is not the probability $P(\mathbf{n}, t|\mathbf{n}_0, t_0)$, but rather another probability function, $p(\tau, \mu|\mathbf{n}, t)\, d\tau$, that represents the probability that if the system has populations at time $t$ given by $\mathbf{n}$ then the next reaction will take place in the interval $[t+\tau, t+\tau+d\tau]$ and will be reaction $R_\mu$, i.e., no reaction will occur between $t$ and $t+\tau$ and the reaction will occur in a $d\tau$ interval immediately afterwards. It is possible to show [8,24] that this function can be written in the form

$$p(\tau, \mu|\mathbf{n}, t) = \{a(\mathbf{n}) \exp[-a(\mathbf{n})\tau]\} \left\{ \frac{c_\mu h_\mu(\mathbf{n})}{a(\mathbf{n})} \right\} . \tag{6}$$

The basic idea of Gillespie's method is to simulate an ensemble of particles $S_i$ that react according to $p(\tau, \mu|\mathbf{n}, t)$ and can be established in the following way [9]

(1) Initialization step. Give initial values for the variables $\mathbf{n}$ and calculate the partial rates $c_\mu h_\mu(\mathbf{n})$ for every reaction $\mu = 1, \ldots, M$.

(2) Monte Carlo step. Generate a random pair $(\tau, \mu)$ that follows the probability density $p(\tau, \mu|\mathbf{n}, t)$ exploiting the fact that it factorizes in parts depending only on $\tau$ and $\mu$ (6). This is done [9,24] by taking two uniform random numbers $r_1, r_2$ in the interval $[0, 1]$ and choosing $\mu$ such that

$$\sum_{i=1}^{\mu-1} c_i h_i(\mathbf{n})/a(\mathbf{n}) < r_1 \leq \sum_{i=1}^{\mu} c_i h_i(\mathbf{n})/a(\mathbf{n}) \tag{7}$$

and $\tau$ such that

$$\tau = -\ln(r_2)/a(\mathbf{n}) . \tag{8}$$

(3) Updating step. Using $(\mu, \tau)$ from the previous step the total time is updated by $\tau$ and the populations of the species involved in reaction $R_\mu$ are updated accordingly with the global stoichiometry of reaction $R_\mu$.

(4) Check the maximum allowed time, and if it has not expired go to the Monte Carlo step.

An important aspect in a stochastic simulation like the present one is the possibility of having a mechanism that allows one to regulate the intensity of the intrinsic or size fluctuations. Of course, the answer is to change the number of reacting particles in the system: the more one has the smaller will be the relative fluctuations. This can be done by changing the volume $V$, remembering to change the $c_\mu$ according to (3). As an illustration, scaling $V$ by 10 implies that the constants $c_\mu$ for bimolecular reactions ($\alpha = 2$) are scaled by 1/10, while unimolecular reactions ($\alpha = 1$) remain unchanged.

## III. RESULTS FOR THE WILLAMOWSKI-RÖSSLER MODEL

In a recent contribution [20] it has been shown that the Willamowski-Rössler model exhibits a noise-induced transition between a strange attractor and a stable fixed point coexisting with it. In this section we shall present the results of a more detailed study, showing how the system may exhibit quite a rich behavior. It is interesting to point out that this model has also been studied by using a recently introduced reactive lattice-gas cellular automaton [10], and that the same kind of intrinsic noise-induced transition has been found [11,12].

First of all, and for completeness, we shall reproduce the chemical and differential equations defining the Willamowski-Rössler [21] mass-action model

$$\begin{aligned} &A_1 + X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2X, \qquad && X + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2Y, \\ &A_5 + Y \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A_2, \qquad && X + Z \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A_3, \\ &A_4 + Z \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} 2Z, \end{aligned} \tag{9}$$

where the species $A_i$ are assumed to remain constant (reagents are continuously introduced and products are retired as they are produced) and the $k_{\pm i}$ are a set of constants that already include the constant terms $A_i$.

The mass-action law allows one to write the evolution equations in the form

$$\begin{aligned} \dot{x} &= k_1 x - k_{-1} x^2 - k_2 xy + k_{-2} y^2 - k_4 xz + k_{-4} \ , \\ \dot{y} &= k_2 xy - k_{-2} y^2 - k_3 y + k_{-3} \ , \\ \dot{z} &= -k_4 xz + k_{-4} + k_5 z - k_{-5} z^2 \ , \end{aligned} \tag{10}$$

where $x$, $y$, and $z$ represent the concentrations, i.e., populations divided by the volume $V$, for the chemical species $X$, $Y$ and $Z$, respectively.

For the parameter values that yield deterministic chaos, the system presents a set of fixed points (with $\dot{x} = \dot{y} = \dot{z} = 0$) that have been numerically determined in Table I: the first two of them are stable while the rest are unstable in some eigendirection. All the fixed points have been presented, even in the case that some of the variables are slightly negative, because stochastic simulations take place in a discrete space in which these deterministic unstable points may become stable with the negative coordinates set to zero.

The result of the stochastic simulations for low to moderate values of the volume $V$, changing the $c_\mu$ by using (3), is that the system performs a noise-induced transition from deterministic, i.e., chaotic, behavior to fixed point, i.e., steady, behavior [see Figs. 1(a) and 1(b) for the cases $V = 10$ and $V = 100$, respectively]. In all the simulations the populations (number of particles) are represented versus time, this time being in arbitrary units, because the values of the constants $k_i$, taken from [21(b)], are arbitrary as they have been chosen with the only requirement of exhibiting deterministic chaos. When the size of the system, i.e., $V$, is increased, the system needs on the average more time to perform this transition, and for some value of $V$ the probability that this transition happens becomes very low, implying that one would need to wait a very long time in order that the transition takes place. In Fig. 1(c) a simulation for $V = 10^3$ is presented in which the system stays described by the strange attractor.

Although the above-mentioned behavior, i.e., transition to fixed point (I), is the most typical, other behaviors are also possible. Figure 2(a) presents a stochastic trajectory that has finished in fixed point (III), while Fig. 2(b) represents another possible behavior as the system becomes trapped in fixed point (IV). In principle, it should be possible that the system ends up in point (II), which is stable, in contrast with points (III) and (IV), which are unstable. However, points (I) and (II) are very close (in both of them the populations of $X$ and $Y$ are very low and for not too large values of $V$ these populations are set to zero in the stochastic evolution). Still a different behavior has been found, although rarely, involving a transition to fixed point (V), which after being discretized corresponds to $(0, 0, 0)$, while no transitions have been so far observed to other fixed points. When all the numbers of particles are zero, one may obtain

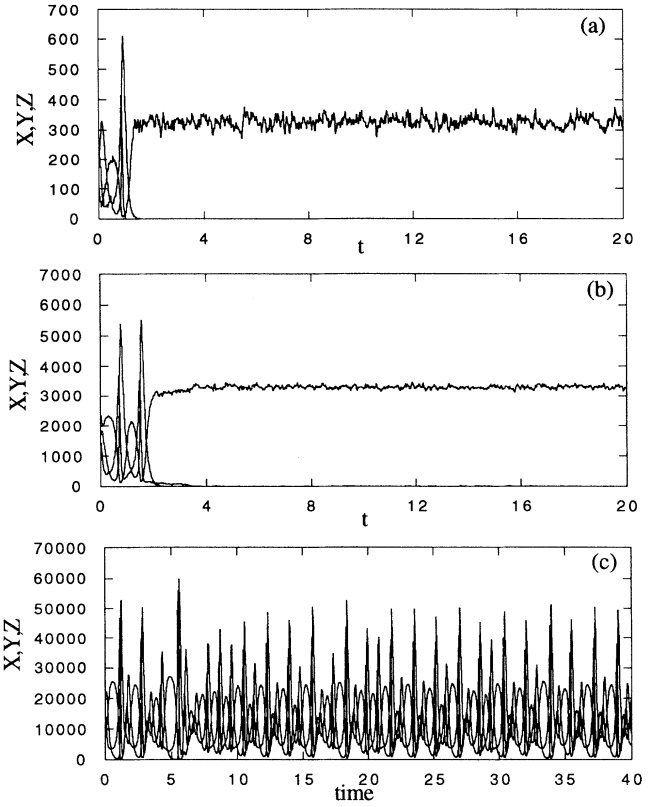


FIG. 1. Time evolution of the populations for species $X$, $Y$, and $Z$ for the Willamowski-Rössler model (10) obtained by stochastic simulation using Gillespie's method. The values of the parameters used here are [21(b)]: $k_1 = 30$, $k_{-1} = 0.25$, $k_2 = 1.0$, $k_{-2} = 0.0001$, $k_3 = 10$, $k_{-3} = 0.001$, $k_4 = 1.0$, $k_{-4} = 0.001$, $k_5 = 16.5$, and $k_{-5} = 0.5$. (a) $V = 10$: the system ends up in fixed point (I) (see Table I); (b) $V = 10^2$: the system ends up in fixed point (I); (c) $V = 10^3$: the system remains in the strange attractor. Time on the abscissas is given in arbitrary units (see discussion in Sec. III), while the quantities on the ordinates represent numbers of molecules.

TABLE I. Coordinates of the fixed points, in chemical concentrations, of the Willamowski-Rössler model (10) and eigenvalues from a linear stability analysis; $s$ means that the equilibrium point is stable while $u$ means unstable. The brackets denote multiplicative powers of ten.

| Point | $x$ | $y$ | $z$ | | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ |
|---|---|---|---|---|---|---|---|
| I | 3.333803[-4] | 1.000033[-4] | 3.299939[1] | $s$ | -16.4997 | -9.99967 | -2.99966 |
| II | 1.714060 | 1.206864[-4] | 2.957195[1] | $s$ | -14.9878 | -8.28594 | -0.22729 |
| III | 1.200000[2] | -8.729860[-6] | 4.882092[-5] | $u$ | -192.2513 | 110.0000 | 58.75121 |
| IV | 1.000271[1] | 2.750714[1] | -1.544709[-4] | $u$ | -1.70128 $\pm$ | 25.73664$i$ | 7.38886 |
| V | -3.333337[-5] | 9.999967[-5] | -6.060583[-5] | $u$ | -10.00003 | 29.99998 | 16.50009 |
| VI | 1.000138[1] | 1.450447[1] | 1.299739[1] | $u$ | -10.0050 | 0.50106$\pm$11.6774$i$ | |

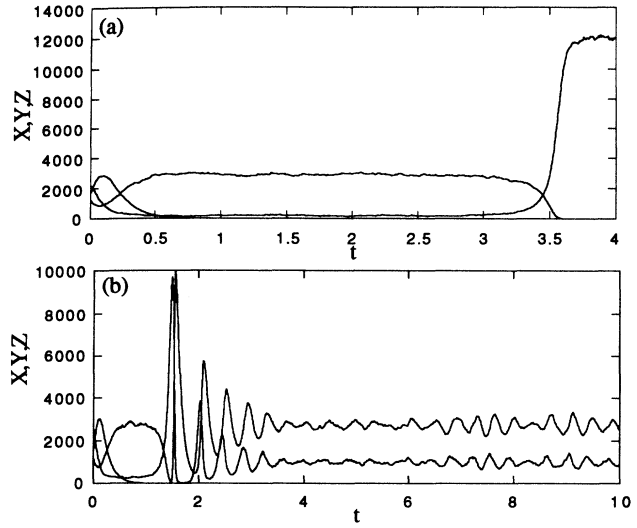


FIG. 2. Time evolution of the populations for species $X$, $Y$, and $Z$ for the Willamowski-Rössler model (10) obtained by stochastic simulation using Gillespie's method and for the constants given in Fig. 1 and by using $V = 100$: (a) the system ends up in fixed point (III) (see Table I); (b) the system ends up in fixed point (IV).

indeterminate results for the time to the next reaction, because the total rate becomes zero and this quantity appears in the denominator of (8).

An interesting issue is to try to model the effects of intrinsic noise as introduced by the stochastic simulations in an easier and simpler way. Motivated by the form of the relative size fluctuations in equilibrium systems, known to scale as $N^{-1/2}$ (see, e.g., [25]), fluctuations with this form have been added to the results of the numerical integration of the differential equations (10) performed through a fourth-order Runge-Kutta procedure [26]. More precisely the populations have been altered in the form

$$n' = n\left(1 + \frac{\gamma\,\sigma[0,1]}{\sqrt{n}}\right) , \tag{11}$$

where $n$ runs over the populations of $X$, $Y$, and $Z$. When performing these calculations one must remember to change the $k_i$ in order to keep size extensivity, through the analogous equation to (3). Here $\gamma$ controls the intensity of the external noise, while $\sigma[0,1]$ (or $N[0,1]$ [24]) is a stochastic variable with Gaussian (or normal) distribution and having zero mean and standard deviation equal to 1.

An important issue when trying to compare both descriptions is the discrete nature of the stochastic simulations. Thus some of the fixed points have concentrations close to zero, and, if $V$ is not too large, the effect of the simulation is to put the population to zero exactly. On the other hand, it was already pointed out that unstable fixed points in the deterministic description become stable in the discrete representation. Accordingly, it is not surprising to find that the use of (11) is not always capable of yielding results analogous to those appearing in the simulations. However, it has been found that if the following trick is implemented the agreement can be almost perfect: in the deterministic evolution with added noise the variables are set to zero if they fall below 1, i.e., real values between zero and 1 are truncated to a value of zero.

As an example, the different behaviors presented in Figs. 1 and 2 have been reproduced by adding external noise of the form (11) to the deterministic evolution. Thus, Fig. 3(a) contains an example of the transition from the strange attractor to fixed point (I), while Fig. 3(b) contains an example of the evolution towards fixed point (III) and Fig. 3(c) an example of the evolution towards fixed point (IV). Notice, however, that even if this *deterministic plus noise* representation is able to capture some elements of the results of the simulations of the chemical master equation, some elements are not included, as happens with the time $\tau$ elapsed between reactions, which is stochastic in (8).

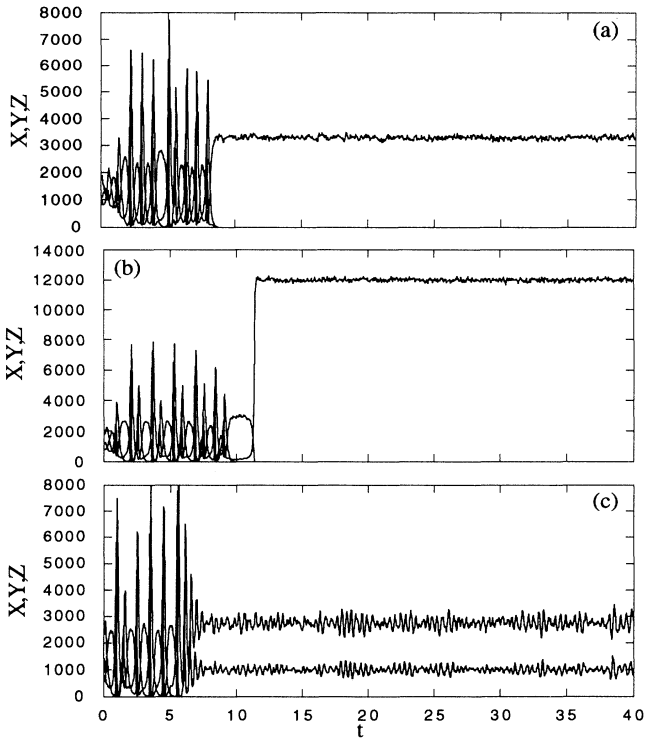


FIG. 3. Time evolution of the populations for species $X$, $Y$, and $Z$ for the Willamowski-Rössler model obtained with numerical integration of (10) after adding an external noise in the form (11) with $\gamma = 0.15$ and for the same constants given in Fig. 1, the variables being scaled by $V = 10^2$: (a) a stochastic trajectory for which the system ends up in fixed point (I), (see Table I); (b) a stochastic trajectory for which the system ends up in fixed point (III); (c) a stochastic trajectory for which the system ends up in fixed point (IV).

## IV. RESULTS FOR A CHEMICAL RÖSSLER MODEL

The number of models that can be written as a set of coupled chemical reactions and that exhibit deterministic chaos is quite small compared to the number of models representing chaos in mechanical, electrical, and other systems. In the latter models the variables may adopt both positive and negative values and it is not possible, in general, to ascribe a chemical mechanism to the differential equations. However, Samardzija *et al.* [22] have shown how to transform a series of nonlinear models in order to obtain models for which the variables are non-negative and the equations can be written in the form of a chemical mechanism.

One of the models considered by these authors is Rössler's [23] prototype of spiral chaos, for which the following mechanism can be written [22]:

$$\begin{aligned} A_1 + X + 2Z &\xrightarrow{k_1} X + 3Z, & X + Y &\xrightarrow{k_2} 2Y \ , \\ A_2 + X + Z &\xrightarrow{k_3} Z + P_1, & A_3 + X + Z &\xrightarrow{k_4} X + P_2 \ , \\ A_4 + 2Y &\xrightarrow{k_5} 3Y, & 2Z &\xrightarrow{k_6} P_3 \ , \\ A_5 + X &\xrightarrow{k_7} 2X, & Y &\xrightarrow{k_8} P_4 \ , \\ A_6 + Z &\xrightarrow{k_9} 2Z \ , \end{aligned} \tag{12}$$

which allows one to write the following evolution differential equations for the chemical concentrations:

$$\begin{aligned} \dot{x} &= -k_2xy - k_3xz + k_7x \ , \\ \dot{y} &= k_2xy + k_5y^2 - k_8y \ , \\ \dot{z} &= k_1xz^2 - k_4xz - 2k_6z^2 + k_9z \ , \end{aligned} \tag{13}$$

assuming that all the $A_i$ and $P_i$ are kept constant throughout the process, their values being included in the rate constants.

In analogous fashion to the case of the Willamowski-Rössler model (see Sec. III), the behavior induced in the system by the presence of intrinsic fluctuations is the transition from the strange attractor to a fixed point coexisting with it. The fixed points of this system, determined numerically by making $\dot{x} = \dot{y} = \dot{z} = 0$ in (13), are presented in Table II. In this case all the fixed points of this system are unstable, at least with respect to one direction. Nevertheless, it is possible that a trajectory remains some time wandering around the fixed point.

An example of the kind of behavior exhibited by the system when intrinsic noise is present can be found in Fig. 4(a), where the system is apparently attracted by point (I). By linearizing the flow in a neighborhood of the fixed point one has that it is contracting along the $Y$ and $Z$ directions while strongly expanding along $X$. This is the behavior observed in Fig. 4(a) after the transient behavior: the population of $X$ grows exponentially while $Z$ dies off to zero. Or, in other words, under the influence of intrinsic fluctuations the system exhibits an explosion in which one of the variables goes to infinity. The behavior shown in Fig. 4(a) is the most typical of the system, in the sense that in a series of simulations most runs exhibit it. Analogously to the Willamowski-Rössler model (see Sec. III) the mean passage time increases when the volume $V$ is increased, the transition becoming highly improbable when $V \to \infty$ (thermodynamic limit).

The system may also exhibit other kinds of behavior. A very curious one is that represented in Fig. 4(b), quite similar in the first part to Fig. 4(a), but where the species that explodes is $Z$. Apparently it cannot be explained by means of a single fixed point. The system seems to perform first a transient being attracted by fixed point (I), but when $X$ increases the simulation falls under the influence of fixed point (II), which is strongly unstable in the $Z$ direction and unstable in the $X$ direction. Thus, although the behavior is different to the previous situation, qualitatively one also has a noise-induced explosion. A different behavior is the one represented in Fig. 4(c) in which the explosion now takes place in $Y$, which probably implies that this behavior is induced by a transition to fixed point (III).

As in the previous section, it is possible to study directly the effect of the addition of noise to the deterministic equations. We first present a time series for a situation in which no external noise has been added [see Fig. 5(a)]. Notice that in the model all the variables have been shifted in order to have non-negative values, including the population of $Z$, which in the original model is either close to zero or then presents a spike. Figure 5(b) presents an example of the effects induced by fluctuations depending on the square root of the number of particles (11): the system explodes after $t = 0.7$. A better detail of this behavior can be obtained from Fig. 5(c), in which an enlargement of the region in which the explosion takes place is shown. As a conclusion of this section it can be said that the presented noise-induced explosive behavior should not be necessarily viewed as the kind of behavior

TABLE II. Coordinates of the fixed points, in chemical concentrations, of the chemical Rössler model (13) and eigenvalues from a linear stability analysis ordered such as to correspond approximately to distortions in the $X$, $Y$ and $Z$ directions, respectively. The brackets denote multiplicative powers of ten.

| Point | $x$ | $y$ | $z$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ |
|---|---|---|---|---|---|---|
| I | 0.0 | 0.0 | 1.000019[2] | 9.999809[1] | -1.20[2] | -1.04802[5] |
| II | 1.047980[2] | 0.0 | 2.0[2] | 2.039780[2] | -1.5202[1] | 1.027542[5] |
| III | 0.0 | 6.0[2] | 1.000019[2] | -5.000019[2] | 1.2[2] | -1.04802[5] |
| IV | 0.0 | 0.0 | 0.0 | 2.0[2] | -1.2[2] | 1.04802[5] |
| V | 0.0 | 6.0[2] | 0.0 | 4.0[2] | 1.2[2] | 1.04802[5] |

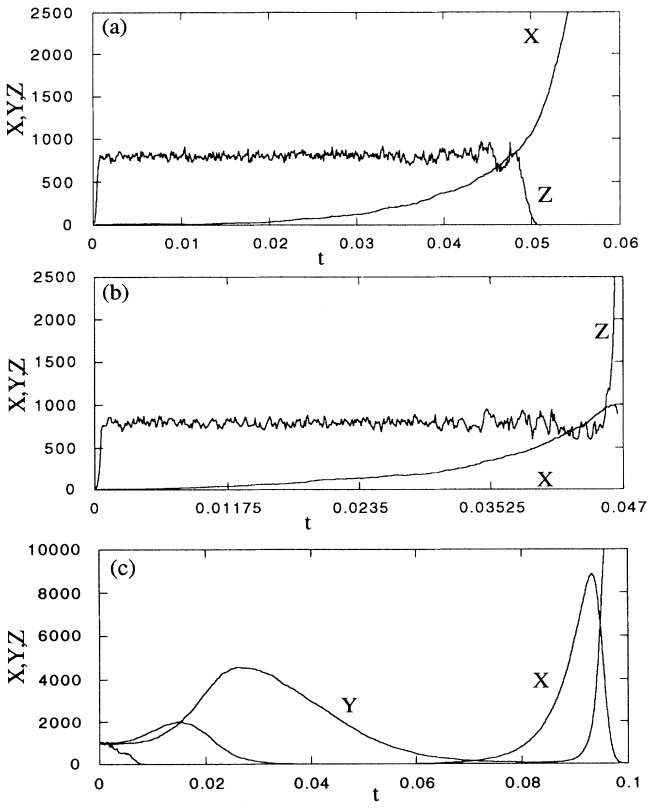


FIG. 4. Time evolution of the populations for species $X$, $Y$, and $Z$ for the chemical Rössler model (13) obtained by stochastic simulation using Gillespie's method and for the following values of the parameters [22]: $k_1 = 1.0$, $k_2 = 1.0$, $k_3 = 1.0$, $k_4 = 100.0$, $k_5 = 0.2$, $k_6 = 52.4$, $k_7 = 200.0$, $k_8 = 120.0$, and $k_9 = 10480.2$, and by using $V = 8$: (a) the system exhibits an explosion in species $X$; (b) the system exhibits an explosion in species $Z$; (c) the system exhibits an explosion in species $Y$. Time on abscissas is given in arbitrary units (see discussion in Sec. III), while the quantities on the ordinates represent numbers of molecules.

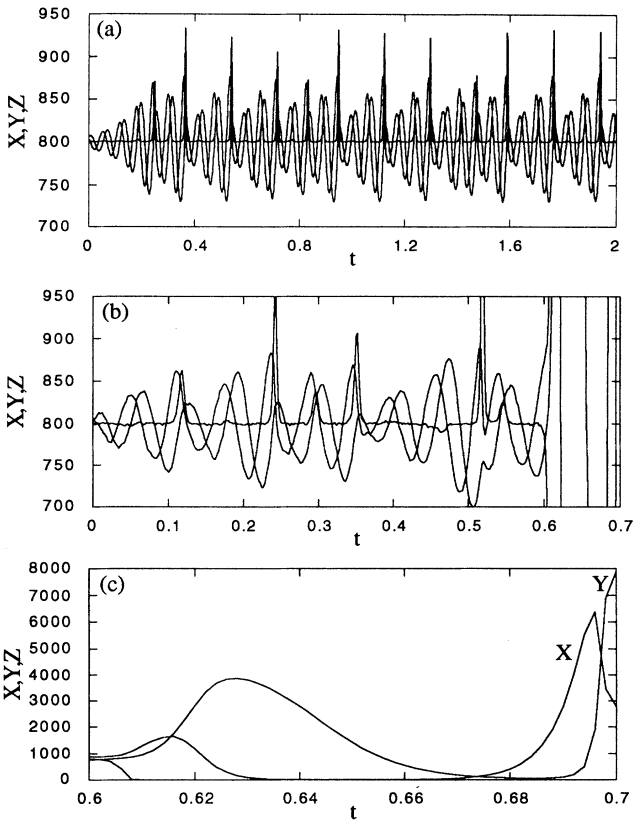


FIG. 5. Time evolution of the populations for species $X$, $Y$, and $Z$ for the chemical Rössler model (13) obtained by numerical integration of (10) and for the constants given in Fig. 4: (a) deterministic evolution; (b) an external noise with the form (11) and $\gamma = 0.008$ is added, the variables being scaled by $V = 8$ and the system exhibits an explosion in species $X$; (c) enlargement of part (b) in the region exhibiting the explosion.

one should expect when fluctuations are applied to the spiral Rössler model. Instead, this particular model offers an example of a transition from a strange attractor to infinity that might be present in other models representing more realistic physical situations.

## V. NOISE-INDUCED TRANSITIONS IN A SIMPLE MODEL

In this section we analyze the two different situations encountered in the previous sections, namely, the intrinsic-noise-induced transition between a strange attractor and a fixed point found in the Willamowski-Rössler model (Sec. III) and the transition between a strange attractor and the escape to infinity (explosion) found in the chemical Rössler model (Sec. IV) by using a simple model. The model is based on the piecewise unidimensional map suggested by Reimann *et al.* [27].

We consider a one-dimensional discrete, i.e., difference equation based, dynamical system coupled to an additive external noise in the form

$$x_{n+1} = f(x_n) + \xi_n, \quad \xi_n = \gamma\,\sigma[0,1]\ , \tag{14}$$

where, as in the case of (11), $\sigma[0,1]$ is a stochastic variable with Gaussian distribution and zero mean and standard deviation equal to 1.

In order to study noise-induced transitions to a fixed point the following model has been used:

$$\begin{aligned} f(x) &= 4\lambda\,(x+2)(x+1) - 2 \quad \text{for} \quad -2 \le x \le -1\ , \\ f(x) &= u(x+1) - 1 \quad \text{for} \quad -1 < x \le -1/2\ , \\ f(x) &= ux \quad \text{for} \quad -1/2 < x \le 0\ , \\ f(x) &= 4\lambda\,x(1-x) \quad \text{for} \quad 0 < x \le 1 \end{aligned} \tag{15}$$

the map being represented in Fig. 6(a). In the absence of external noise the system dynamics takes place only in the interval $[-1,0]$. However, if external noise is added the system has some probability of leaving this inter-

val, and for this reason two logistic maps have been added at the two extremes at a parameter value yielding a fixed point behavior ($\lambda = 0.72$). Thus this system (15) effectively models the transitions observed in the Willamowski-Rössler model of Sec. III [see Fig. 6(a)].

Another version allowing escape to infinity has also been considered:

$$f(x) = \begin{cases} u(x+1) - 1 & \text{for } -\infty < x \leq -1/2 \ , \\ ux & \text{for } -1/2 < x < \infty \ , \end{cases} \tag{16}$$

the map being represented in Fig. 6(b). This behavior is analogous to the one observed for the chemical Rössler model of Sec. IV [see Fig. 6(b)].

In the original work [27] noise-induced transitions occur when additive Gaussian noise is added to the original piecewise map. To see the different effect of noise in the context of our previous results, we have scaled the system variable $x$ by a factor $a$, this playing the role of volume $V$ in the two previous sections, and having the effect of decreasing the relative importance of noise. Figs. 7(a)– 7(c) contain a study for different values of the factor $a$ scaling the system variable for the model displayed in Fig. 6(a). Thus, Fig. 7(a) contains the result for $a = 1$, for which the system performs the transition after some time. In Fig. 7(b) the same is done for the case $a = 5$: the system still performs the transition, but clearly the fluctuations around the fixed point are smaller. Finally, for $a = 10$ and for the number of iterations considered the transition does not take place, this being the approach to the *thermodynamic* limit. Nevertheless, it must be pointed out that when $a$ is increased, although the time that one needs to wait before the transition takes place can be very high, the transition will take place if one waits enough time. Instead, in the case of the purely deterministic evolution this transition is impossible.

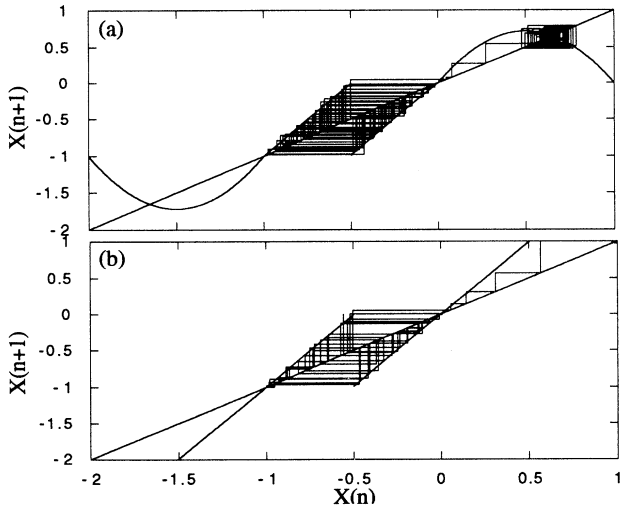


FIG. 6. Unidimensional maps based on the work by Reimann *et al.* [27] with the presence of additive noise (14) with $\gamma = 0.04$: (a) this map (15) models noise-induced transitions to a fixed point and has $u = 1.98$ and $\lambda = 0.72$ as the parameter of the two logistic equations (they exhibit a fixed point); (b) in this map (16) the presence of noise induces the escape to infinity ($u = 1.98$).

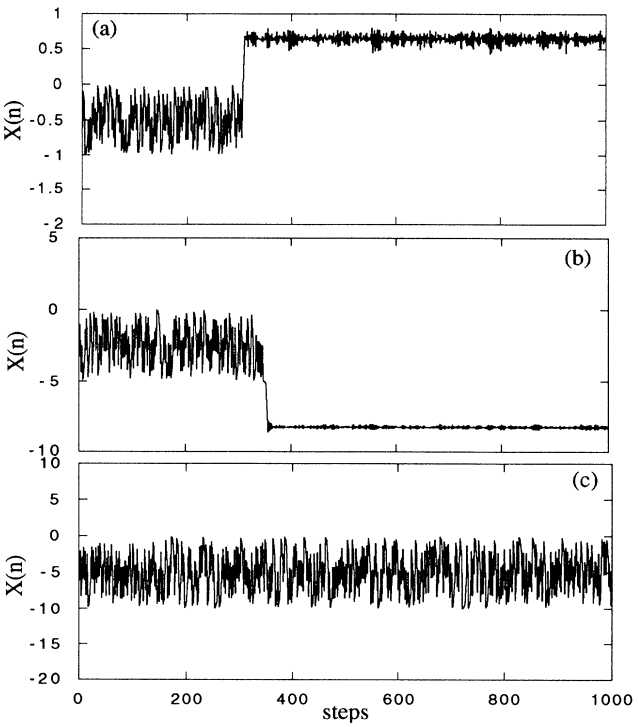


FIG. 7. Time evolution of the system variable $x$ for the map represented in Fig. 6(a) with additive noise and where the system variable is scaled through the following values: (a) $a = 1$; the system exhibits a transition to the fixed point; (b) $a = 5$; the same happens but the relative weight of the fluctuations is smaller; (c) $a = 10$; no transition is present after the iterations considered. For the values of the parameters, see Fig. 6(a).

In turn, similar results are represented in Fig. 8 for the model considered in Fig. 6(b). In Figs. 8(a) and 8(b) the system escapes to infinity when one considers $a = 1$ and $a = 5$, through the different branches of the map, respectively. Instead, for $a = 10$ the system does not escape for the number of iterations considered [see Fig. 8(c)].

## VI. CONCLUSIONS

One of the features of many dynamical systems, written either as differential equations or as maps, is the coexistence of several attractors in the system (see, e.g., [1]). Although the basin of attraction of one of these attractors may fill most of the phase space volume, making it improbable that a random initial condition ends up in any of the competing attractors, the presence of noise may alter the picture considerably, namely, by allowing the system to switch from one to another attractor. In this work, we have analyzed the effect of intrinsic noise, caused by the finite size of the system, on systems exhibiting deterministic chaos, but with one or more co-

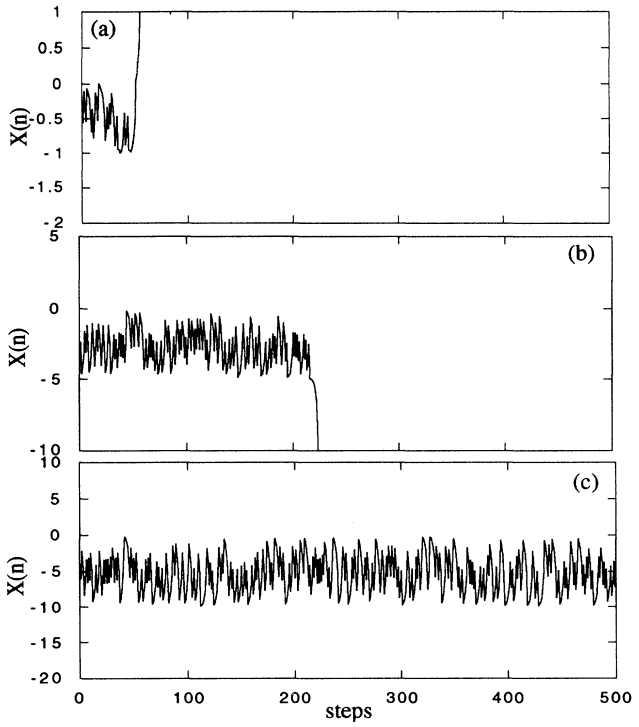


FIG. 8. Time evolution of the system variable $x$ for the map represented in Fig. 6(b) with additive noise and where the system variable is scaled through the following values: (a) $a = 1$; the system escapes to infinity; (b) $a = 5$; the system escapes to infinity; (c) $a = 10$, the system stays in the attractor after the iterations considered. For the values of the parameters, see Fig. 6(b).

existing fixed points to which the system may switch. The intrinsic (or thermodynamic) fluctuations can be incorporated by going beyond the usual differential equation description in terms of purely macroscopic variables and employing instead a mesoscopic description in which a coarse-graining process over the detailed microscopic evolution is performed.

The mesoscopic description has been carried out through a method suggested by Gillespie [9] that allows one to study coupled chemical reactions by means of a Monte Carlo simulation of the corresponding chemical master equation in which the chemically reactive events are considered through discrete jump processes. The systems studied in this way are spatially homogeneous and the whole process is considered to be Markovian, implying that for each reactive event many nonreactive collisions must occur in order that, locally, the system obeys the Maxwell-Boltzmann distribution law for the velocities.

The systems considered in this work have been the Willamowski-Rössler model [21], the chemical representation of the Rössler model [23] due to Samardzija *et al.* [22], and two extensions of the simple map model due to Reimann *et al.* [27]. The first model has been shown to exhibit transitions to some of the fixed points of the flow, even to originally unstable points that are stabilized by the discrete nature of the mesoscopic representation. This representation tends, in principle, to the deterministic one in the sense that the times needed to perform the transition become longer, although a few transitions have still been observed for relatively high values of particles. The second model offers an example of a noise-induced explosion, showing that if one is seeking to suppress chaos the effect of noise may yield an even less controlled system behavior.

The physical meaning of the results presented and the plausibility of these transitions has been reinforced by showing that the same kind of transitions can be obtained by resorting to a Langevin-type treatment, namely, by integrating the evolution differential equations and adding to the variables a term of noise proportional to the square root of the number of particles, as suggested by equilibrium statistical mechanics. Moreover, a simple model in which the presence of alternative fixed points is included from the beginning is considered in two versions, each one of them resembling the behavior of one of the flows. It must be pointed out that for the Willamowski-Rössler the same kind of noise-induced transition has been found by Wu and Kapral [11,12] through the use of a reactive lattice-gas cellular automaton, which also performs a mesoscopic representation of the system.

Regarding the debate [13,16] about the relevance of intrinsic noise effects in chaotic systems and the usefulness of the phenomenological representation, the conclusion of the present work is that in the case where multiple attractors compete with the strange attractor the deterministic equations alone are not able to predict the behavior of the system in the limit of long times. However, not every system having a positive Lyapounov exponent exhibits this behavior, as shown in recent work for systems that do not have other competing attractors [18] and also by other authors [11,12,17].

Well-stirred coupled chemical reactions exhibiting low-dimensional deterministic chaos are examples of systems with sustained nonequilibrium behavior (through the appropriate continuous feeding of reagents). Thus this kind of transition may be considered as an analogue in far from equilibrium systems of the well-known phase transitions of equilibrium statistical mechanics. Although the transitions might occur in small to intermediate size domains, these could act as nucleation centers to induce a transition in the whole system. Of course, the study of the whole effect would imply the consideration of spatial coordinates, e.g., through the use of a reactive lattice-gas cellular automaton, that has been shown [11,12] to behave locally like the chemical master equation.

## ACKNOWLEDGMENTS

We acknowledge Professor S. Velasco and Dr. J.A. White for their useful comments about the manuscript, Professor L. Pesquera and Dr. M.A. Rodríguez for suggesting to us the use of an external noise scaling as $\sqrt{n}$, and Professor R. Kapral and Dr. P. Reimann for making their work available to us before publication. This work was supported by DGICYT (Spain) Research Grants No. PB92-0279 (J.G.) and No. PB92-0295 (M.A.M.).

[1] E. Ott, *Chaos in Dynamical Systems* (Cambridge University Press, Cambridge, England 1993).
[2] B.L. Hao, *Chaos II* (World Scientific Press, Singapore, 1989).
[3] S.K. Scott, *Chemical Chaos* (Oxford University Press, Oxford, 1991).
[4] *Microscopic Simulations of Complex Flows*, edited by M. Mareschal (Plenum, New York, 1990).
[5] G.A. Bird, *Molecular Gas Dynamics* (Clarendon, Oxford, 1976).
[6] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).
[7] C.W. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1983).
[8] D.T. Gillespie, Physica A **188**, 404 (1992).
[9] D.T. Gillespie, J. Comput. Phys. **22**, 403 (1976); J. Phys. Chem. **81**, 2340 (1977).
[10] D. Dab, A. Lawniczak, J.P. Boon, and R. Kapral, Phys. Rev. Lett. **64**, 2462 (1990); R. Kapral, A. Lawniczak, and P. Masiar, *ibid.* **66**, 2539 (1991); J. Chem. Phys. **96**, 2762 (1992); D. Dab, J.P. Boon, and Y.X. Lee, Phys. Rev. Lett. **66**, 2535 (1991); X.G. Wu and R. Kapral, Physica A **188**, 284 (1992).
[11] X.-G. Wu and R. Kapral, Phys. Rev. Lett. **70**, 1940 (1993); J. Chem. Phys. **100**, 5936 (1994); Phys. Rev. E **50**, 3560 (1994).
[12] X.-G. Wu and R. Kapral, Ann. N.Y. Acad. Sci. **706**, 186 (1993); in *Chemical Waves and Patterns*, edited by R. Kapral and K. Showalter (Kluwer, Dordrecht, 1994).
[13] R.F. Fox and J.E. Keizer, Phys. Rev. Lett. **64**, 249 (1990); Phys. Rev. A **43**, 1709 (1991); R.F. Fox, *ibid.* **41**, 2969 (1990); **42**, 1946 (1990).
[14] J.E. Keizer and J. Tilden, J. Phys. Chem. **93**, 2811 (1989); J.E. Keizer and R.F. Fox, Phys. Rev. A **46**, 3572 (1992); R.F. Fox and T.C. Elston, Chaos **3**, 313 (1993).
[15] C. Bracikowski, R.F. Fox, and R. Roy, Phys. Rev. A **45**, 403 (1992).
[16] G. Nicolis and V. Balakrishnan, Phys. Rev. A **46**, 3569 (1992).
[17] P. Geysermans and G. Nicolis, J. Chem. Phys. **99**, 8964 (1993).
[18] M.A. Matías and J. Güémez, J. Chem. Phys. **102**, 1597 (1995).
[19] J.P. Crutchfield, J.D. Farmer, and B.A. Huberman, Phys. Rep. **92**, 45 (1982).
[20] J. Güémez and M.A. Matías, Phys. Rev. E **48**, R2351 (1993).
[21] (a) K.D. Willamowski and O.E. Rössler, Z. Naturforsch. Teil A **35**, 317 (1980); (b) B.L. Aguda and B.L. Clarke, J. Chem. Phys. **89**, 7428 (1988).
[22] N. Samardzija, L.D. Greller, and E. Wasserman, J. Chem. Phys. **90**, 2296 (1989).
[23] O.E. Rössler, Phys. Lett. **57A**, 397 (1976).
[24] D.T. Gillespie, *Markov Processes* (Academic Press, New York, 1992).
[25] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).
[26] W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes,* 2nd ed. (Cambridge University Press, Cambridge, England, 1992).
[27] P. Reimann, R. Müller, and P. Talkner, Phys. Rev. E **49**, 3670 (1994).