On the effects of molecular fluctuations on models of chemical chaos

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In this work the effects of molecular or intrinsic fluctuations on some models of coupled chemical reactions exhibiting low-dimensional deterministic chaos are investigated. The study is performed by considering the system at the mesoscopic level, namely by stochastically simulating the corresponding chemical master equation. Two specific models are studied: the isothermal three-variable autocatalator of Peng et al. and a chemical version of Rössler’s model of spiral chaos. The main conclusions are that the corresponding strange attractors obtained in these models are robust against fluctuations, although when the system is near the onset of chaos the presence of fluctuations may anticipate the appearance of chaos. © 1995 American Institute of Physics.

I. INTRODUCTION

The emergence of coherent structures like sustained oscillations and deterministic chaos are good examples of organized behavior in far from equilibrium macroscopic systems.1,2 This kind of behavior can be described by means of phenomenological equations in terms of the relevant macroscopic variables, but a very intriguing aspect is the emergence of this organized behavior out of the myriads of intrinsically random collision events that occur when the system is viewed at the molecular level. In this work we shall deal with chemical reactions exhibiting oscillations, chaos, etc.3 of which the Belousov–Zhabotinsky reaction is probably the best known example.

The motivation for having a closer look into the emergence of these phenomena by going beyond the usual phenomenological (or macroscopic) approach is not only academic, but at least in the case of systems displaying chaotic behavior. Low-dimensional chaotic systems are characterized by having at least one positive Lyapunov exponent, indicating sensitive dependence on the initial conditions. Fox and Keizer4 have carried out an analysis of the importance of intrinsic (or size) fluctuations on chaotic systems by means of a linearization of the fluctuations around their mean value. The conclusion is that molecular fluctuations grow as the largest Lyapunov exponent, implying that some after some time the uncertainties in the macroscopic variables are as large as the variables themselves. These results imply that the usual deterministic description is inadequate for chaotic systems and some experimental results5 have confirmed that molecular fluctuations may have this dramatic effect.

On the other hand, Nicolis and co-workers6 have performed an analysis of these fluctuations arriving to the conclusion that the strange attractor on which the time evolution occurs after all transients have died out is robust against the presence of fluctuations, describing this attractor the most probable behavior of the system. This is compatible with the fact that individual trajectories can be strongly affected by the presence of molecular fluctuations.

In principle, it is possible to simulate directly this kind of nonequilibrium processes from first principles through molecular dynamics techniques (see, e.g. Ref. 7), but the calculations are quite cumbersome. The main reason is that a typical molecular event occurs in a subpicosecond time scale, while chemical oscillations typically take place in a time scale of the order of some minutes, i.e., they remarkably differ in 15 orders of magnitude, approximately. On the other hand, the algorithm spends most of the computer time in collecting very detailed information about the collisional processes, while most of these collisions are elastic, being the reactive events relatively rare.

Thus, one finds motivation for an intermediate way of dealing with the problem, namely by resorting to a mesoscopic description, intermediate between the microscopic and macroscopic perspectives. In principle, the easiest and simplest way of tackling the problem would be to add a stochastic term to the phenomenological equations to obtain a Langevin-type of description.8 However, this approach is completely phenomenological and one would like to use a more soundful approach, and, in particular, one that does not rely on the validity of a given linearization procedure. In this work we shall perform simulations that employ a mesoscopic representation, being the idea to take care of the actual occurrence of the reactive processes. Thus, one performs a coarse-graining procedure in which the information about the elastic processes and many fine details about the reactive collisions is skipped, concentrating the method only on the occurrence of reactive events, that are relatively rare compared to the elastic ones. When comparing to the macroscopic representation what this representation is doing is to introduce fluctuations and correlations among the particles of the reacting species.

Two such mesoscopic methods have been so far suggested in the literature. This work is based on the use of the so-called master equation1,8,9 that governs the time evolution of the reaction probability. This method is restricted to the study of homogeneous, i.e., space-independent or well-stirred systems. It can be shown10 that the so-called chemical master equation, that treats chemical reactions as discrete Markov jumps in the space of the populations for every species, is based on firm grounds from the point of view of collision theory, provided that elastic processes are much
more probable than reactive collisions and, thus, that the process can be considered Markovian. This technique has been used to study the effects of intrinsic fluctuations in homogeneous, i.e., well-stirred, systems by some groups,\textsuperscript{11,12} while a study of an extended system has also appeared.\textsuperscript{13} Chemically reactive systems are the natural and classical candidates for the master-equation treatment because, in the simplest case, the way in which molecules collide in an elementary step determines the macroscopic equations through the mass-action law and the three levels of representation, micro-, meso- and macroscopic, are interconnected. However, a master-equation representation of hydrodynamic systems has been recently introduced.\textsuperscript{14}

The second approach relies on the use of a lattice-gas cellular automaton,\textsuperscript{15} of which a variety able to deal with reactive situations has been also introduced.\textsuperscript{16} Some applications to the study of the effect of molecular fluctuations on chaos have been carried out by Wu and Kapral.\textsuperscript{17,18} The method deals quite naturally with systems of spatial coordinates due to its lattice structure, while it can be shown that the time evolution at each of its nodes is completely analogous to that of the chemical master equation.\textsuperscript{17} In particular, the automaton rules can be defined in such a way that one obtains directly the well-stirred situation.\textsuperscript{17} In summary, the main virtues of this representation are the possibility of treating the well-stirred and nonhomogeneous cases within the same method and the possibility of performing extensive calculations in a very efficient and essentially exact form, especially in parallel machines, due to the distributed character of the automata and the fact that one performs only integer and boolean operations.

The aim of this work is to try to elucidate the role of molecular fluctuations in models of coupled chemical reactions in homogeneous conditions such that only temporal variations need to be considered. This is the case considered in previous contributions.\textsuperscript{11,12,17,18} We may anticipate that the results for the two models considered in this contribution, when they are in the chaotic regime are qualitatively quite close to the predictions of Nicolis \textit{et al.}\textsuperscript{5} In a more quantitative fashion, Wu and Kapral\textsuperscript{17,18} have exploited the strongly dissipative character of the dynamics, either deterministic or stochastic, to approximately represent the system as a one-dimensional return map, such that one can obtain the invariant distribution of the system, and also the associated measure. In this sense, it is the perturbed, i.e., stochastic, dynamics on the attractor that is relevant and the consequent change in the invariant measure. The effects of intrinsic fluctuations are much more important if the system is in the middle of period-doubling cascade. As shown by Wu and Kapral,\textsuperscript{17,18} when looking at the corresponding Poincaré section, the effect of intrinsic noise in this case is to make the system explore the unstable manifold of the corresponding unstable fixed point, that originates from the original limit cycle of the flow, and that is embedded in the strange attractor. The strange attractor itself is the closure of this unstable manifold. When the noise strength is high, the dynamics will strongly resemble that of the strange attractor itself, although with most of the fine details being lost.

Nevertheless, in recent contributions,\textsuperscript{12,17,18} it has been shown that a novel behavior can appear for systems in which the strange attractor coexists with other attractor, because the system may exhibit intrinsic noise-induced transitions from the strange attractor towards the other competing attractor. In particular, this kind of behavior becomes dominant in the case that the size of the system is small or moderate. In any case, this mechanism suggests that in the case of large systems an interplay between intrinsic and stirring noise may appear, making possible the transition to the fixed point in a small region that may act as a nucleation center for the whole system, exhibiting the neighboring regions the same kind of transition in a gradual way. Thus, the results presented in the remaining of this work may be typical results for chaotic systems that do not have competing attractors and that are not near the onset of a chaotic transition.

In this work, the study of the effects of intrinsic noise will be carried out by using the stochastic method put forward by Gillespie\textsuperscript{19} to allow the Monte Carlo simulation of the chemical master equation, or more precisely of a slight reformulation of the latter in which the probability of occurrence of the next reaction is simulated (see Sec. II). Moreover, it will be shown that some nontrivial features in the chemical mechanisms of the reactions considered in this work, namely the use of scaling factors for the reaction rates and the alternance of fast and slow processes, can be easily overcome within the method.

The plan of this article is as follows. Sec. II presents a brief account of the method employed to simulate the chemical master equation. Section III contains an application to the three-variable autocatalator model devised by Peng \textit{et al.}\textsuperscript{20} Then, in Sec. IV the method suggested by Poland\textsuperscript{21} to allow writing models of chaos as a set of coupled chemical reactions is applied to the model of spiral chaos introduced by Rössler.\textsuperscript{22} The paper closes in Sec. V with the conclusions of this work.

II. METHOD

The procedure employed in this work to account for molecular fluctuations relies on Gillespie’s method,\textsuperscript{19,23} that affords a Monte Carlo simulation of the chemical master equation arising when one writes chemically reactive events as discrete jump probabilistic processes. The chemical master equation is the time evolution equation for the conditional probability $P(n,t|n_0,t_0)$ that if the population of the chemical species, written as a vector $n=(n_1,...,n_N)$, is $n_0$ at time $t_0$ then it will be $n$ at time $t$. In practice, Gillespie’s method does not simulate the above \textit{grand} probability $P(n,t|n_0,t_0)$, but rather the probability density $p(n,t|n_0,t)$, that represents the probability that, if the system has populations at time $t$ given by $n$, then the next reaction will take place in the interval $[t+t,t+t+d t]$, being reaction $R_\nu$.

The aim is to describe a system with a series of reaction channels $R_\nu(\mu=1,...,M)$

\begin{equation}
\nu_1 S_1 + \nu_2 S_2 + \cdots + \nu_i S_i + \cdots \rightarrow \nu_1 S_1 + \nu_2 S_2 + \cdots + \nu_i S_i + \cdots
\end{equation}
open for the existing species $S_i$ with stoichiometric coefficients $v_i$ to react. 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 $[t, t+dt]$. In order to obtain the rate for reaction $R_\mu$, one needs to know the number of different possible combinations of the reactant molecules, $h_\mu$, that can be written in the form,

$$h_\mu = \frac{n_1!}{(n_1-v_1)!} \times \frac{n_2!}{(n_2-v_2)!} \times \cdots$$

(2)

being the product extended to all reagents in (1), and $n_i$ the number of molecules of the $S_i$ species with stoichiometric coefficient $v_i$. From this quantity the rate of reaction for channel $R_\mu$ takes the form $a_\mu = c_\mu h_\mu$, being written the total rate as,

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

(3)

It is possible to compare this stochastic representation of a chemical reaction with the usual deterministic treatment in which reaction rates are written from the chemical mechanism through the mass-action law, e.g. for reaction $R_\mu$ (1), in the form $k_\mu x_i x_j \cdots$. First of all, it is necessary to notice that the deterministic rate is written in terms of intensive variables (chemical concentrations), i.e., $x_i = n_i/V$ (where $V=VN_A$ includes already Avogadro's number, as for these tiny volumes in macroscopic terms these reduced units are more convenient), while the stochastic kinetics depends on extensive variables: the $n_i$. For convenience, in the rest of the work we shall write down the volume in reduced units, i.e., $V=V_i$.

The two representations coincide in the limit that the number of particles is large, provided that one includes the corresponding volume terms when defining $c_\mu$,

$$c_\mu = k_\mu V^{1-a_\mu}$$

(4)

being $a_\mu$ the order of reaction for channel $R_\mu$, $a_\mu = \sum v_i$, where the sum is extended to all the reagents of reaction $R_\mu$. The way of regulating the intensity of fluctuations consists in varying the system size (or volume), as the long-term behavior (the attractors) are defined in terms of the intensive variables. In the thermodynamic limit ($N \to \infty$, $V \to \infty$, $N/V =\text{finite}$) fluctuations should vanish. In purity, expression (2) should represent combinations and, thus, an additional term $v_i!$ should appear dividing every factor, because the particles are to be considered indiscernible. However, this would imply the presence of analogous factors multiplying the r.h.s. of (4), with the consequence that these factors would cancel out in the calculation of the total (or partial) rate in (3). Therefore, we have chosen to present simplified expressions for $h_\mu$ and $c_\mu$.

The probability density $p(\tau, \mu | n, t)$ can be written in the form,

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

(5)

being written as a product of a factor depending on $\tau$ and another one depending on $\mu$. The whole procedure consists of the Monte Carlo simulation of the reacting process subject to the probability function (5), and can be represented by the following steps:

1. Initialization step: give initial values for the variables $n$.
2. Monte Carlo step: calculate the partial rates $c_\mu h_\mu(n)$ for every reaction $\mu=1,\ldots,M$ and generate a random pair $(\tau, \mu)$ accordingly to the probability distribution $p(\tau, \mu | n, t)$. This is done by taking two uniform random numbers $r_1$ and $r_2$ in the interval $[0,1]$, and choosing $\mu$ such that

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

(6)

and $\tau$ such that

$$\tau = -\ln(r_2)/a(n)$$

(7)

using the so-called inverse function method to generate the corresponding stochastic variable.

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

4. Decision step: check the maximum allowed time, and if it has not expired go to the Monte Carlo step.

An interesting issue is to try to model in a simple way the effects of intrinsic noise as introduced by the stochastic simulations in an easier and simpler way, namely by using a stochastic equation of the Langevin type. Motivated by the form of size fluctuations in equilibrium systems, known to scale as $N^{1/2}$ (see e.g. Ref. 24), a stochastic term with this form has been added to the results of the numerical integration of the corresponding differential equations (performed through a standard fourth order Runge–Kutta procedure). More precisely the system variables are altered in the form,

$$x_i' = x_i + \gamma \sigma[0,1] \sqrt{x_i}$$

(8)

at the end of every integration step. Here $\gamma$ controls the intensity of the external noise, while $\sigma[0,1]$, or $N(0,1)$, is a stochastic variable of zero mean and with a Gaussian (normal) distribution with amplitude one. The reliability of (8) will be tested in further sections by comparing it with the results of the stochastic simulations. In order to allow a closer comparison with the simulations once a value of $\gamma$ is established it is not further changed, and rather the size (volume) of the system is changed through $V$. In fact, scaling by $V$ is equivalent to scaling $\gamma$ by $1/\sqrt{V}$. In the case of the deterministic description, that depends only on the chemical concentrations (that are intensive variables), scaling with $V$ does not change the description, altering only the number of particles present by $V$.

### III. STUDY OF THE AUTOCATALATOR MODEL

The three-variable isothermal autocatalator model was introduced by Peng, Scott, and Showalter as a model of...
deterministic chaos in a model of coupled chemical reactions. The scheme consists of six reaction steps,

\[ \begin{align*}
A & \rightarrow X, \quad A + Z \rightarrow X + Z, \\
X & \rightarrow Y, \quad X + 2Y \rightarrow 3Y, \\
Y & \rightarrow Z, \quad Z \rightarrow P.
\end{align*} \]

(9)

From these chemical steps the following evolution equations can be obtained by straightforward application of the mass-action law,

\[ \begin{align*}
\dot{x} &= k_1 + k_2 z - k_3 x - k_4 x y^2, \\
\dot{y} &= k_3 x + k_5 x y^2 - k_6 y, \\
\dot{z} &= k_5 y - k_6 z,
\end{align*} \]

(10)

representing \( x \), \( y \), and \( z \) the corresponding concentrations of species \( X \), \( Y \), and \( Z \).

Figure 1(a) shows the result of a typical deterministic evolution with \( V = 1 \) exhibiting periodic behavior. In turn, Fig. 2(a) presents a stochastic simulation with \( V = 1 \) exhibiting the same kind of cycles seen in the deterministic result, although alternating with higher cycles. When the simulation is performed by using \( V = 0 \) [see Fig. 2(b)], the approximately regular cycles still alternate with some higher one, although not so high as for \( V = 1 \). When the level of fluctuations is reduced, e.g. in Fig. 2(c) with \( V = 50 \), the result is closer to the deterministic one, being the result approximately periodic.

Analogous results can be obtained by adding external noise in the form of \( \sim \). Thus, Fig. 1(b) contains one of these runs with \( \gamma = 0.065 \) and \( V = 1 \) in which several high oscillations are observed, in analogy to Fig. 2(a). On the other hand, in Fig. 1(c) a run is plotted with the same value of \( \gamma \) and \( V = 10 \), being the result somehow close to Fig. 2(b). Instead, Fig. 1(d) offers an example of the gradual transition towards the thermodynamic limit (\( V = 50 \) has been used in this case). The simulation presented in Fig. 2(a) is an example of the effect of intrinsic noise on a system in which the basin of attraction of a limit cycle is not steep, being instead somehow excitable. It must be stressed that the deterministic description is not able to retrieve this feature.

In order to obtain deterministic chaos with fewer parameters in the chemical mechanism (9), Peng, Scott, and Showalter introduced a transformation of variables from which the following evolution equations can be obtained,
\[
\begin{align*}
\dot{x} &= \kappa + \mu z - x - xy^2, \\
\sigma \dot{y} &= x + xy^2 - y, \\
\delta \dot{z} &= y - z,
\end{align*}
\]

in which the four parameters \(\kappa, \mu, \sigma,\) and \(\delta\) are written in terms of the original constants.\(^{20}\) The main difference between (10) and (11) is that in the latter case the \(\dot{y}\) and \(\dot{z}\) are multiplied by the parameters \(1/\sigma = k_2/k_3 = 200\) and \(1/\delta = k_4/k_5 = 50\), allowing this to achieve in a clearcut way a separation in the timescales in which these species evolve.

From the point of view of the implementation of Gillespie’s method, one can consider (11) as formally being derived from (9), by making the association \([k_1] = \kappa, [k_2] = \mu, [k_3] = 1, [k_4] = 1, [k_5] = 1,\) and \([k_6] = 1,\) where the brackets mean that the constants in the chemical mechanism (9) that are in the l.h.s. are replaced by those values in the r.h.s. One must also take into account the coefficients \(\sigma\) and \(\delta\) multiplying the l.h.s. of \(\dot{y}\) and \(\dot{z}\) in order to reproduce the deterministic results. This will imply that every time a reaction whose mass action law term appears in the r.h.s. of \(\dot{y}\) and/or \(\dot{z}\), then the population of the scaled species \(Y\) and/or \(Z\) should be updated by \(1/\sigma = 200\) and \(1/\delta = 50\) times, respectively, the normal prescription of the method. It could be argued that this procedure is not very chemical, in the sense that the occurrence of a given reaction makes the population of \(Y\) increase/decrease by 200 and the population of \(Z\) by 50, but this is the only way in which the simulations can be carried out. In addition, the stochastic coefficient \(\epsilon_\mu\) corresponding to constant \([k_1]\) must be scaled in the appropriate form with \(V\), namely as \(1/V^2\), and thus cannot be considered identically one. This problem does not appear with the other reactions having a constant equal to one, because they are unimolecular.

Taking \(\mu\) as the bifurcation parameter and keeping the other parameters constant, the model (11) exhibits a Feigenbaum period doubling route to chaos, and several different conditions have been considered, namely values of \(\mu\) for which the system is in the road to chaos and values of \(\mu\) in the chaotic regime. The first case considered is \(\mu = 0.1\) for which the system exhibits periodic behavior, see Fig. 3(a), although it is in the middle of a period-doubling window.\(^{20}\) The effect of intrinsic noise is to anticipate the appearance of chaos, as can be seen in Fig. 4(a) for \(V = 10^2\) and in Fig. 4(b) for \(V = 10^4\). When the size of the system is increased to \(V = 10^4\), see Fig. 4(c), the system looks less chaotic (in the \(V \rightarrow \infty\) limit it approaches the thermodynamic limit and the behavior is periodic). Analogous results are obtained for this system when external noise in the form (8) is added to the system. Three different situations for which the effect of noise ranges from strong (inducing chaos) to moderate can be found in Figs. 3(b)–3(d) for \(V = 10^2\), \(V = 10^3\) and \(V = 10^4\), respectively.

These results are similar to the effect of external noise on nonlinear systems in the road to chaos\(^{26}\) and with the conclusions of Nicolis et al.\(^{6}\) In a more quantitative fashion, Wu and Kapral\(^{17,18}\) have discussed the effects of internal noise on prechaotic situations in the case of the Willamowski–Rössler model by noticing that this kind of noise destabilizes the periodic orbit, and the system starts making excursions along the corresponding unstable manifold of the periodic orbit, that spans the strange attractor. The authors have also put these conclusions in a quantitative way through the analysis of the corresponding invariant distribution, both in the deterministic and stochastic cases, considering both external and internal noise.

In order to investigate the effects of fluctuations on truly chaotic conditions, the same kind of study has been performed for \(\mu = 0.154\). Figure 5(a) shows the deterministic evolution of the system for this set of parameters. On the other hand, several simulations have been performed for several values of the system volume starting from the same initial condition. Figures 6(a)–6(c) shows the results for \(V = 10^2\), \(V = 10^3\), and \(V = 10^4\), respectively. The result is that the system stays chaotic, being roughly described by the same strange attractor although individual trajectories differ due to the effect of noise, as proved by Fox et al.\(^{4}\) However, the most probable behavior, described in terms of the strange attractor, does not change much, as advocated by Nicolis

FIG. 3. Time evolution of the number of particles for the species \(X, Y,\) and \(Z\) for the scaled isothermal three-variable autocatalator (11) obtained by numerical integration after adding an external noise in the form (8). The values of the parameters used here are: \(\kappa = 10, \delta = 0.02, \sigma = 0.005,\) and \(\mu = 0.1:\) (a) \(V = 10^2\) and \(\gamma = 0\) (deterministic evolution); (b) \(V = 10^2\) and \(\gamma = 0.1;\) (c) \(V = 10^4\) and \(\gamma = 0.1;\) (d) \(V = 10^4\) and \(\gamma = 0.1.\)
et al. Of course, not all the details of the fine structure of the strange attractor are conserved, depending on the relative strength of noise, as discussed in Ref. 26. This is in contrast with the results obtained in the case that the strange attractor coexists with one or more fixed points, where the intrinsic fluctuations can induce transitions from the strange attractor to a fixed point. By including external noise in the form ~8!, one obtains results that are similar to the stochastic simulations, as shown in Figs. 5~b!–5~d! for the same values of V considered in Figs. 6~a!–6~c!.

IV. STUDY OF A CHEMICAL FORM OF THE 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 mechanical, electrical, hydrodynamic, and other systems that exhibit this behavior. In the latter type of 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, Poland has shown how to transform a series of non-linear 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. The method recalls soundful ideas from chemical kinetics, namely the presence of slow steps that determine the rate followed by fast reactions that complete the global stoichiometry.

Here we shall consider Rössler’s prototype of spiral chaos, for which the following mechanism can be written:

\[
\begin{align*}
R &\rightarrow X, \quad A + Y \rightarrow A^* + Y \text{ (slow)}, \\
A^* + X &\rightarrow A + R \text{ (fast)}, \quad A + Z \rightarrow A^* + Z \text{ (slow)}, \\
A^* + X &\rightarrow A + R \text{ (fast)}, \quad B + X \rightarrow B^* + X \text{ (slow)}, \\
B^* &\rightarrow Y \text{ (fast)}, \quad B + Y \rightarrow 2Y, \\
C &\rightarrow C^* \text{ (slow)}, \quad C^* + Y \rightarrow C + R \text{ (fast)}, \\
R &\rightarrow Z, \quad Z \rightarrow R, \\
D + X + Z &\rightarrow X + 2Z.
\end{align*}
\]

FIG. 4. Time evolution of the number of particles for the species \(X, Y,\) and \(Z\) for the scaled isothermal three-variable autocatalator \((11)\) obtained through stochastic simulation using Gillespie’s method and for the constants given in Fig. 3: (a) \(V = 10^2\); (b) \(V = 10^3\); (c) \(V = 10^4\).

FIG. 5. Time evolution of the number of particles for the species \(X, Y,\) and \(Z\) for the scaled isothermal three-variable autocatalator \((11)\) obtained by numerical integration after adding an external noise in the form \(\sim \delta\). The values of the parameters used here are: \(k = 10, \quad \delta = 0.02, \quad \sigma = 0.005, \quad \mu = 0.154\); (a) \(V = 10^2\) and \(\gamma = 0\) (deterministic evolution); (b) \(V = 10^2\) and \(\gamma = 0.1\); (c) \(V = 10^3\) and \(\gamma = 0.1\); (d) \(V = 10^4\) and \(\gamma = 0.1\).
that allows to write the following evolution differential equations for the reaction intermediates $X$, $Y$, and $Z$,

$$
\begin{align*}
\dot{x} &= k_1 - k_3 y - k_2 z, \\
\dot{y} &= k_4 x + k_5 y - k_6, \\
\dot{z} &= k_7 - k_8 z + k_9 x z,
\end{align*}
$$

(13)

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

Regarding the implementation of Gillespie’s method, in the case of the chemical mechanism (12) it must be taken into account that in the slow/fast couples the species appearing in the evolution equations are the ones present in the slow reaction, while in the updating step in Gillespie’s algorithm one has to consider the joint stoichiometry of the couple. Like in the previous section, we shall first consider a prechaotic behavior, i.e., a set of parameter values for which the system is the road to chaos, in this case in the middle of a period-doubling cascade. $k_8$ is the control parameter that has been chosen for this system, and in Fig. 7(a) a time series obtained from numerical integration of the deterministic equations is presented for the case $k_8 = 17.5$. After a transient, one has regular oscillations, with the number of particles of $X$ and $Y$ separated only by phase and $Z$ exhibiting spikes in regular intervals, as in the original Rössler model. Next, the system has been studied by using Gillespie’s method for different values of the volume $V$. Thus, Fig. 8(a) presents a stochastic simulation for $V=10$. In this case the effect of intrinsic noise is to make the system explore a larger volume of phase space, giving the system a more chaotic appearance. By increasing $V$ the system resembles more the purely deterministic evolution, although with some background noise [see Fig. 8(b) for $V=10^2$]. If the size of the system grows even more, as in Fig. 8(c) for $V=10^3$, most of the noise effects disappear, but the evolution is not completely regular yet.

Like in the previous section, results obtained by adding external noise with the form (8) are presented. Thus, Fig. 7(b) presents the evolution obtained with $\gamma=0.065$ and $V=10$. This evolution resembles to some extent the one obtained with Gillespie’s method and presented in Fig. 8(a). In analogous way, Fig. 7(c) contains the results obtained with $V=10^2$, that, again, can be compared to Figure 8(b). Still another condition is the one shown in Fig. 7(d), that be compared to the true simulation of Fig. 8(c). The conclusion is that with both methods one obtains results that are qualitatively similar, and that announce the sensitivity of prechaotic systems to the effects of intrinsic noise in agreement with the conclusions presented in Sec. III.

We shall now analyze the effect on noise when the be-
behavior of the system is chaotic, that for this model can be achieved with $k_5 = 20.7$ (Ref. 21). Figure 9(a) contains a time series obtained from numerical integration of (13), being represented the number of particles of $X$, $Y$, and $Z$ for $V = 10$. In analogy to the behavior of the original model exhibiting spiral chaos, species $X$ and $Y$ oscillate together, differing only by a phase, although careful observation shows that these oscillations are not regular. When $X$ and $Y$ reach a certain threshold, variable $Z$ activates returning $X$ and $Y$ to the inner part of the oscillation. Simulations of this model through Gillespie’s methods are presented in Fig. 10, being part (a) the $V = 10$ case, for which the effect of noise is quite intense and the spiral structure of the attractor is altered in some moments. Fig. 10(b) presents a simulation for $V = 10^2$ in which the system follows more closely the strange attractor, although some noise induced effects are still observable. Instead, for the simulation with $V = 10^3$ presented in Figure 10(c) the effect of intrinsic noise on the system is almost negligible in the timescale considered.

Like in the previous section, it is possible to obtain results completely analogous to those given by the Gillespie’s model by altering in the variables in the form (8) in the deterministic evolution resulting by integrating the evolution equations (13). Figure 9(b) presents one of these situations for a high level of noise ($\gamma = 0.1$ and $V = 10$), and made to exhibit some resemblance with the stochastic simulation with $V = 10$. In turn, Fig. 9(c) presents a calculation with $V = 10^2$ resembling the $V = 10^2$ stochastic simulation [Fig. 10(b)]. To conclude, Fig. 9(d) contains the result of applying external noise in the case $V = 10^3$, leading to result that can be considered indistinguishable from the deterministic evolution of Figure 9(a). Another chemical representation of the Rössler model due to Samardzija et al. was considered in a recent study, offering an example of a noise-induced explosion (transition to infinity). In such representation all the three variables are made positive (the opposite could not represent a chemical reaction), forcing $Z$ to take values in the same range than $X$ and $Y$. In the model considered here, that was suggested by Poland, $Z$ presents a value near zero most of the time, with occasional spikes, and we believe that this behavior is more realistic and akin to the spirit of Rössler’s model.

V. CONCLUSIONS

A very intriguing problem in the study of systems exhibiting order in macroscopic scales far from equilibrium conditions is the interplay between this organized behavior and their naturally erratic appearance when seen at the molecular level. As the timescales associated to these two lev-
els, macroscopic and microscopic, differ by many orders of magnitude, a sensible approach is to pursue a mesoscopic representation, where a coarse-graining process of the uninteresting details of the molecular collisions is performed. The mesoscopic representation carried out in this work consists in the stochastic simulation of the chemical master equation by employing a method introduced by Gillespie, allowing 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 as Markov discrete jump processes. The systems studied in this fashion are spatially homogeneous and, as the whole process is considered to be Markovian, this implies that for each reactive event many nonreactive collisions must occur. This allows to study the effects of molecular fluctuations on systems that can be written in terms of a set of deterministic nonlinear evolution laws.

The systems considered in the present work have been the three-variable isothermal autocatalator model and the chemical representation of the Rössler model due to Poland. The effect of intrinsic fluctuations on limit cycles exhibiting a relatively flat basin of attraction is that the system performs relatively long excursions around the attractor. However, when the system is close to a period-doubling bifurcation the effect of intrinsic noise is to anticipate the appearance of chaos, smearing part of the fine structure of the subharmonic cascade. On the other hand, for systems exhibiting a well-established chaotic regime molecular fluctuations change the detailed behavior of the system, but not the most probable distribution, that remains centered around the strange attractor, although it may lose some of its fine structure.

These conclusions agree with the work of Nicolis et al. about the effects of intrinsic fluctuations on chaotic systems. However, if one considers the effects of noise on individual trajectories, the property of sensitivity to initial conditions exhibited by chaotic systems avoids any prediction of the future state of the system, as established by Fox et al. Moreover, it has been shown that the effects of intrinsic fluctuations due to the finite size of the system yield similar results to the introduction of external noise scaling as the square root of the number of particles, in the spirit of a Langevin-type treatment. In any case, the stochastic simulation of the master equation is the genuine representation of the effect of fluctuations at the macroscopic level, incorporating features like the correct time step between successive reactions that are not present in any formulation based on the solution of the deterministic equations. It is to be noticed that conclusions that are similar to those obtained from the present results, including the, to some extent, equivalent effects of external and internal noise, have been obtained for a different, although analogous, model by Wu and Kapral through the use of a reactive lattice-gas cellular automaton.

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