RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 48, NUMBER 4 OCTOBER 1993

Internal fluctuations in a model of chemical chaos

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 28 June 1993)

The effect of internal fluctuations in chaotic systems is studied for the case of the Willamowski-Rössler model. In this system the strange attractor coexists with a stable fixed point, and it is shown that internal fluctuations may induce a transition between these two situations. Simulations are performed with the stochastic method due to Gillespie [J. Comput. Phys. **22**, 403 (1976); J. Phys. Chem. **81**, 2340 (1977)], and the conclusions are verified by representing the intrinsic fluctuations in the form of a multiplicative external noise.

PACS number(s): 05.45.+b, 05.40.+j, 82.20.Fd, 82.40.Bj

The study of systems described by nonlinear evolution laws has afforded the concept of deterministic chaos, allowing one to look at many phenomena from a new perspective in such disparate fields as fluid mechanics, ecology, economics, etc. Nonlinear dynamical systems (with at least three variables) showing chaos exhibit sensitive dependence on the initial conditions and present universal routes leading to chaos. Usually one describes these systems in terms of a small number of macroscopic variables, supposed to be the most relevant for the problem. In this approach one neglects the microscopic structure of the system, which may induce the presence of fluctuations and correlations that are referred to as internal, intrinsic, or thermodynamic fluctuations (or noise).

Very little is known about the relevance of these intrinsic fluctuations in the description of deterministic chaotic systems. However, one can mention the studies by Fox and Keizer [1,2] showing how in some cases the presence of fluctuations may induce a breakdown in the usual deterministic description in terms of macroscopic variables. Some other recent studies are those due to Nicolis and co-workers [3,4], who have found, by solving directly the master equation, that a deterministic description in terms of macroscopic variables may still be useful in the study of the behavior of the most probable value (instead of the mean value). These conclusions find support in the lattice-gas cellular-automaton simulations performed by Wu and Kapral [5].

The purpose of this work is to show that the inclusion of intrinsic fluctuations may change the observable behavior in some chaotic systems, and more precisely in those systems in which the strange attractor coexists with a locally stable fixed point, such as in the Willamowski-Rössler [6] model of chemical chaos. Some chemical reactions involving autocatalysis are good examples of deterministic chaos [7], with the advantage that the evolution differential equations can be written in a simple way if one knows the chemical mechanism of the reaction. On the other hand, the effect of fluctuations in a chemical reaction can be analyzed if one writes the chemical master equation, where the chemical reactions are considered in terms of birth and death processes. In the present work we have used the stochastic method suggested by Gillespie [8], which consists in a simulation of the chemical master equation.

The Willamowski-Rössler [6] mass-action model can be represented by the following chemical equations:

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

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 include the constant terms A_i. The mass-action law allows one to write the evolution equations in the form

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

where x, y, and z represent the populations for the chemical species X, Y, and Z. Typical values for x, y, and z can be seen in Fig. 1, where a phase portrait of the strange attractor has been plotted for the values of the constants $k_{\pm i}$ given in [6(b)]. This plot has been obtained by solving parametrically Eqs. (2) as a function of time.

The method suggested by Gillespie allows one to study well-stirred systems for which diffusion terms can be neglected, while the chemical master equation is simulated stochastically by assuming that it can be written as a Markov chain. This assumption is valid in the case that nonreactive encounters are more probable than reactive collisions [9]. This assumption is quite reasonable in the case of this system, because X, Y, and Z are intermediate species in the reaction for which the populations (or concentrations) take a small value compared to reagents and products A_i. In the stochastic simulation [8] one needs

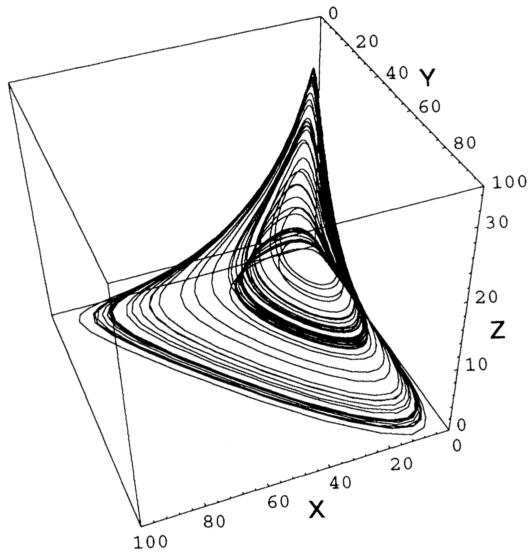

FIG. 1. Three-dimensional phase space representation for the Willamowski-Rössler model (2). The values of the parameters used here are [6(b)]: $k_1 = 30$, $k_{-1} = 0.25$, $k_2 = 1.0$, $k_{-2} = 0.0001$, $k_3 = 10$, $k_{-3} = 0.001$, $k_4 = 1.0$, $k_{-4} = 0.001$, $k_5 = 16.5$, $k_{-5} = 0.5$. The initial conditions are $x_0 = 10$, $y_0 = 10$, and $z_0 = 5$.

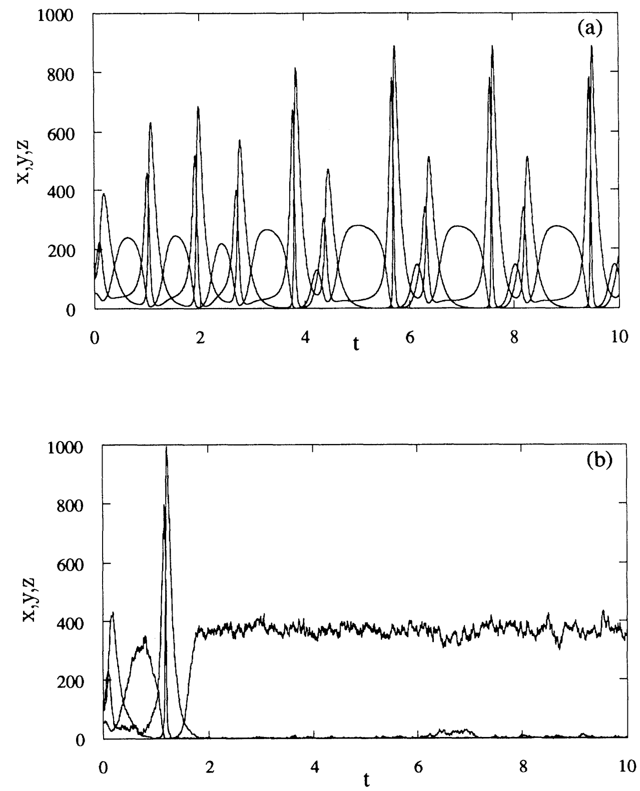

FIG. 2. Time evolution for the species x, y, and z for the constants given in Fig. 1 and scaling the populations by $a = 10$ (see text): (a) deterministic [solution of Eqs. (2)]; (b) result of a simulation with the stochastic method due to Gillespie. The initial conditions are $x_0 = 100$, $y_0 = 100$, and $z_0 = 50$.

to generate two uniform random numbers in the interval [0, 1] which decide the reaction of the mechanism taking place at every moment and the time interval τ that the reaction needs to take place. These numbers have been generated by using the algorithms described in Chap. 7 of Ref. [10].

In the original formulation of Gillespie's method it is not possible to change the intensity of the fluctuations, as one always works with the number of *molecules* produced by the rate coefficients. However, this intensity can be regulated by conveniently scaling the populations x, y, and z. If one wishes to scale all the populations by some constant a, it is very easy to check that the rate coefficients that correspond to bimolecular steps must be scaled by $1/a$, i.e., k_{-1}, k_2, k_{-2}, k_4, and k_{-5}, while the coefficients k_{-3} and k_{-4} need to be scaled by a, and the other coefficients (unimolecular) remain unchanged.

The result of the stochastic simulation for the constants and initial conditions of Fig. 1 and for different values of a ranging from 1 to 1000 is always that the populations of every species become steady. This corresponds to a stable fixed point [11] that for the original constants ($a = 1$) has been characterized as having $x_s = 0.000\,33$, $y_s = 0.000\,10$, $z_s = 32.999$, these numbers being scaled by a in the same way as the populations. A linear stability analysis at these conditions shows that the fixed point is stable, having the eigenvalues $(-3.00, -10.00, -16.50)$.

In Fig. 2 the time evolution for the variables x, y, and z for the case $a = 10$ is shown. In Fig. 2(a) the solution obtained by numerically integrating (2) by using the Runge-Kutta method (Ref. [10], Chap. 16) is plotted. In Fig. 2(b) the result of the stochastic simulation using the method of Gillespie is presented for the same conditions. It can be seen that the effect of intrinsic fluctuations is to make the system switch from the chaotic behavior shown in part (a) to a regular evolution in (b), although some background noise is present. The value of z does not match exactly the solution of the fixed point, i.e., $z_s = 329.99$, because the discrete nature of the simulation makes $x = y = 0$.

To reinforce the plausibility of these results, we have solved the deterministic evolution equations (2) in the presence of a multiplicative external noise. This noise alters the populations in the following way:

$$x' = x + \gamma\,\sigma[0,1]\,\sqrt{x} \qquad (3)$$

and analogously for y and z, where γ regulates the intensity of the noise and $\sigma[0,1]$ is a stochastic variable of mean zero and with a Gaussian distribution of amplitude one, different for x, y and z. The form of this noise comes from the remark that thermodynamic fluctuations depend on the square root of the populations [12].

Figure 3 shows the time evolution of the system populations for the same constants used in Fig. 2, in the presence of an external noise of the form (3). The addition of this noise yields a behavior that is completely analogous to the one obtained with the stochastic simulation method, as can be seen by comparing Figs. 2(b) and

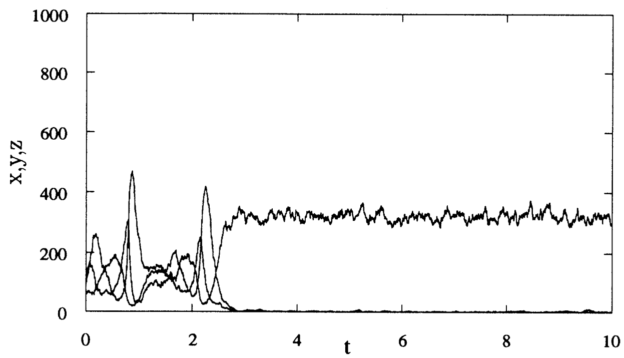

FIG. 3. Time evolution for the species x, y, and z after adding an external noise in the form (3) with $\gamma = 0.065$ and for the same constants and initial conditions of Fig. 2.

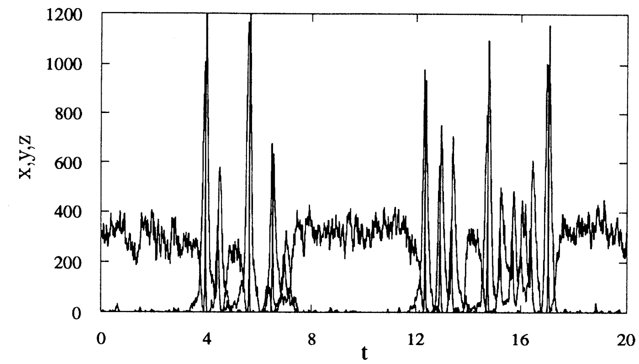

FIG. 4. Time evolution for the species x, y, and z by adding noise in the form (3) with $\gamma = 0.20$, for $a = 10$ and initial conditions $x_0 = 1$, $y_0 = 1$, and $z_0 = 330$, i.e., in the basin of attraction of the fixed point.

3. These results are not dependent on the precise form of (3), and the use of a standard multiplicative noise, scaling as x, yields the same results for different values of γ, although (3) should be more physically sound. It is interesting to point out that the use of higher noise intensities γ can invert this transition, making the system switch back and forth between the fixed point and the strange attractor, as shown in Fig. 4.

By performing an analogy with well known concepts used in the study of phase transitions, we could say that we have found an example of a probability distribution presenting two maxima: one associated with the strange attractor and the other with the stable fixed point (the latter being higher). In the absence of fluctuations, if the system shows deterministic chaos, the probability distribution will always remain centered around the strange attractor. However, if fluctuations are present, there is a mechanism to switch to the most probable situation, as happens in a phase transition.

It is quite difficult to establish whether this kind of coexistence appears in other chaotic systems or rather is quite unique. We have not found this behavior in other three-variable systems [13], but it could be more common in systems with a higher dimensionality. The Willamowski-Rössler model is characterized by having two variables (x and y) that adopt values close to zero in some cycles [see Figs. 1 and 2(a)]. The small value of these species makes intrinsic (or size) fluctuations very important, and as these variables fall below some critical value the system becomes attracted by a fixed point that exists nearby.

In conclusion, in this work we have shown for the Willamowski-Rössler model of chemical chaos that internal fluctuations may induce a transition from a chaotic dynamical behavior driven by a strange attractor to a steady state behavior, driven by a stable fixed point. Internal fluctuations have been introduced through the stochastic simulation method due to Gillespie. These conclusions have been reinforced by introducing an external noise in the deterministic equations with the same form as thermodynamic fluctuations.

We acknowledge Professor S. Velasco and Dr. J. A. White for their useful comments about the manuscript, and Professor L. Pesquera and Dr. M. A. Rodríguez for suggesting to us the use of an external noise scaling as $\sqrt{x}$. This work was supported by the DGICYT (Spain) Research Grants No. PG92-0279 (J.G.) and PB92-0295 (M.A.M.).

[1] R.F. Fox and J.E. Keizer, Phys. Rev. Lett. **64**, 249 (1990); Phys. Rev. A **43**, 1709 (1991).
[2] R.F. Fox, Phys. Rev. A **41**, 2969 (1990); **42**, 1946 (1990).
[3] G. Nicolis and V. Balakrishnan, Phys. Rev. A **46**, 3569 (1992).
[4] P. Peeters and G. Nicolis, Physica A **188**, 426 (1992).
[5] X.-G. Wu and R. Kapral, Phys. Rev. Lett. **70**, 1940 (1993).
[6] (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).
[7] S.K. Scott, *Chemical Chaos* (Oxford University Press, Oxford, 1991).
[8] D.T. Gillespie, J. Comput. Phys. **22**, 403 (1976); J. Phys. Chem. **81**, 2340 (1977).
[9] D.T. Gillespie, Physica A **188**, 404 (1992); *Markov Processes* (Academic Press, New York, 1992).
[10] W.H. Press, S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes*, 2nd ed. (Cambridge University Press, Cambridge, 1992).
[11] There is a second stable fixed point with coordinates $(1.7141, 0.00012, 29.5719)$ for $a = 1$, but no stochastic simulation has finished in it.
[12] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York 1965).
[13] J. Güémez and M.A. Matías (unpublished results).