Internal Fluctuations and Deterministic Chemical Chaos

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The effects of internal noise on chaotic and periodic dynamics of a chemical system are investigated. Calculations are carried out for a mesoscopic model of the Willamowski-Rössler reaction, a mass-action model that displays deterministic chemical chaos. The model incorporates internal fluctuations that arise from the reactive and diffusion processes in the system. The character of the noisy dynamics is analyzed and questions related to the validity of deterministic models in the chaotic regime are discussed. The interplay among spatial degrees of freedom, system size, and internal fluctuations are studied for this chaotic dynamical system.

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Low-dimensional chaos in dissipative dynamical systems is one of the most widely investigated topics in nonlinear dynamics. Its ubiquity in a variety of physical contexts and the fact that a few well-characterized scenarios describe its onset have been responsible for the intense activity on its origin and properties.

Chemically reacting systems have provided some of the most clear-cut examples of deterministic chaos [1]. The theoretical description of low-dimensional chaos is based on the ordinary nonlinear differential equations of mass action kinetics, constrained in some way to maintain the system out of chemical equilibrium. This description assumes that the chemical system is well stirred and that inhomogeneities arising from incomplete mixing or internal fluctuations do not affect the basic features of the phenomenon.

Deterministic chaos manifests itself as a structured aperiodic motion of the trajectory of the system in the phase space of the macroscopic chemical concentrations. This macroscopic chaotic dynamics has its origin in the molecular reactive and elastic collision processes in the system, and the effects of local concentration fluctuations that arise from these collisional events must be accounted for in a full description of the chaotic dynamics. When the deterministic system is chaotic, fluctuations can have pronounced effects on the dynamics since nearby phase points diverge exponentially with a mean growth rate given by the maximum Lyapunov exponent. The effects of external noise on chaotic dynamics have been studied in some detail [2]. Internal noise arising from the molecular nature of the system is also expected to have important effects but here the problem is more subtle. Fox and Keizer [3] pointed out that that the growth of intrinsic fluctuations is governed by the Jacobi matrix, which also determines the Lyapunov exponents. They argue that the macroscopic rate law loses its meaning since fluctuations grow to macroscopic size and are comparable to the mean values of the macroscopic dynamical variables. This interpretation has been questioned by Nicolis and Balakrishnan [4].

In order to investigate this problem one must describe the system at a level that goes beyond the deterministic chemical kinetic equations. Both master equations [4] and approximate Fokker-Planck equations [3] have been used for this purpose. Here we employ the reactive lattice-gas automaton method [5] to construct a mesoscopic description of a reacting system whose underlying chemistry gives rise to deterministic chaos. This approach is based on lattice-gas methods formulated for hydrodynamics [6] and in the reactive case can be viewed as a type of implementation of the master equation method. Consequently, internal molecular fluctuations and spatial degrees of freedom are naturally incorporated in the description. In this Letter we study the interplay of internal molecular fluctuations, spatial degrees of freedom and system size, and their effects on the structure of macroscopic, deterministic, chemical chaos. Our calculations provide rather direct information on the effects of internal noise on systems that manifest deterministic chemical chaos and, therefore, can be used to discuss the questions posed above concerning the validity of the macroscopic description within the context of the automaton dynamics.

While numerous model chemical rate equations exhibit deterministic chaos, from a microscopic perspective it is especially interesting to focus on models whose mass action kinetics, as embodied in a chemical mechanism that reflects the microscopic forward and reverse reactive collision processes, is capable of yielding chaotic dynamics. A model introduced by Willamowski and Rössler [7] is of this type. The reaction mechanism involves only bimolecular steps and is given by

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

where $\mathcal{K} = \{k_{\pm i} :\ i = 1, \ldots, 5\}$ is a set of forward and reverse rate constants. In order to force the system out of equilibrium the concentrations of the set of species $\mathcal{A} = \{A_j :\ j = 1, \ldots, 5\}$ are assumed to be constant. In this circumstance the mass action rate law is

$$\begin{aligned} \dot{x} &= \kappa_1 x - \kappa_{-1}x^2 - \kappa_2 xy + \kappa_{-2}y^2 - \kappa_4 xz + \kappa_{-4} \, , \\ \dot{y} &= \kappa_2 xy - \kappa_{-2}y^2 - \kappa_3 y + \kappa_{-3} \, , \\ \dot{z} &= -\kappa_4 xz + \kappa_{-4} + \kappa_5 z - \kappa_{-5}z^2 \, , \end{aligned} \tag{2}$$

and elements of the set $\kappa = \{\kappa_{\pm i} \colon i = 1, \ldots, 5\}$ are scaled rate constants that incorporate the constant concentrations of the $\mathcal{A}$ species. Since the concentration phase space is three dimensional, the possibility of deterministic chaos exists and its properties and the mechanism of its appearance have been studied [7,8].

The reactive lattice-gas automaton model corresponds to a coarse graining of the full reactive molecular dynamics [5]. We suppose that all reactive species are dilute in some solvent so that nonreactive (elastic) collisions occur primarily with the solvent molecules. In the automaton these elastic collisional events are modeled in the following way: The automaton collision dynamics takes place on three hexagonal lattices, one for each of the $X = 1$, $Y = 2$, and $Z = 3$ species. Each node of a lattice can have a maximum of six particles of a species, with velocities in the six lattice directions. The motions of the solvent molecules are not followed explicitly, instead collisions with the solvent are assumed to randomize the velocities of the chemical species at each discrete time step. (The constrained species $\mathcal{A}$ are taken into account through the reactive collision frequencies of the X, Y, and Z species.) Every automaton particle is assigned a discrete position, velocity, and species label. At each time step the molecules move in directions determined by their velocities to neighboring nodes of the lattice and their velocities are randomized. Thus, nonreactive dynamics is modeled by a random walk with exclusion. Reactive events are determined by a reaction probability matrix $\mathbf{P}$ which couples the dynamics on the lattices. It specifies how a configuration at a node consisting of $(\alpha_1, \alpha_2, \alpha_3)$ numbers of each species changes as a result of the reactions in (1) and its elements are determined from the reaction mechanism, consistent with the exclusion principle. The mean-field description of the automaton can be constructed explicitly [5] and the reaction velocities are polynomials in the average concentrations. For a suitable choice of $\mathbf{P}$ the automaton mean-field equation can be identified with the phenomenological mass-action rate law (2). This identification does not restrict the full automaton dynamics to the mean-field limit; it simply means that if the dynamics is such that the mean-field approximation is valid the automaton dynamics will yield the standard deterministic mass-action kinetics. This feature is essential in the analyses presented below since it allows us to assess the importance of internal fluctuations on the dynamics and to compare the automaton results, which contain the full effects of the interplay between reaction and diffusion, with a known mean-field result which ignores such fluctuations. Thus, within this automaton universe that mimics the kinetics of the Willamowski-Rössler model we can study the validity of the mass-action rate law. There is another important advantage to this construction: To the extent that this mean-field description is valid, one can explore automaton models that correspond to specific parameter ranges of the rate law. Hence, just as the parameter set κ can be tuned to yield a variety of attracting states, a series of automaton models can be constructed to investigate these attracting states.

We consider first reactive and elastic collision frequencies and system sizes such that molecular diffusion is able to maintain homogeneity over the entire unstirred system and a macroscopic description in terms of ordinary differential equations is applicable. The automaton simulation of "deterministic" chaotic dynamics is given in Fig. 1 which shows the attractor in the 3D concentration phase space. The simulation was carried out on a set of 100×100 lattices and the concentrations were obtained by averaging over the nodes of the lattice. The internal fluctuations have important but anticipated effects on the dynamics: They cause the phase-space flow to spread in the unstable directions along the attractor "manifold" but produce little change in the thickness of the attractor in the strongly contracting directions transverse to the flow. The eigenvalues associated with the unstable fixed point [9] are $\lambda_1 = -15.4152$ and $\lambda_{2,3} = 1.6672 \pm i7.9020$, indicating a strong contraction of the flow along one eigendirection and a weaker expansion of the flow along the other eigendirections. The Poincaré map, shown in Fig. 2, has a linelike character indicating preservation of the sheetlike structure of the attractor; however, there is strong dephasing of the intersections of

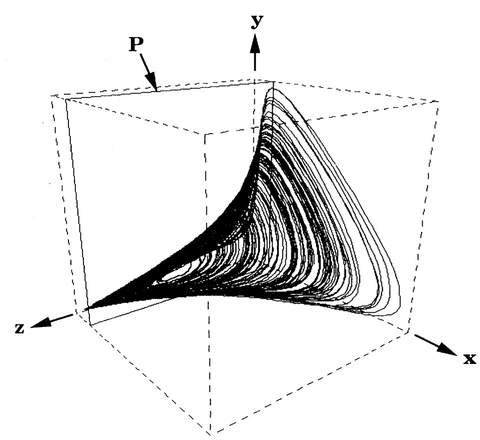

FIG. 1. Chaotic attractor. Parameters are $\kappa_1 = 31.2$, $\kappa_{-1} = 0.2$, $\kappa_2 = 1.572$, $\kappa_{-2} = 0.1$, $\kappa_3 = 10.8$, $\kappa_{-3} = 0.12$, $\kappa_4 = 1.02$, $\kappa_{-4} = 0.01$, $\kappa_5 = 16.5$, and $\kappa_{-5} = 0.5$. The dashed box which contains the attractor has one corner at the origin of the coordinate system, $(x, y, z) = (-0.02599, -0.05498, -0.08193)$, and corners lying along the x, y, and z axes at 2.51039, 2.25439, and 4.77463, respectively. The Poincaré section is labeled P.

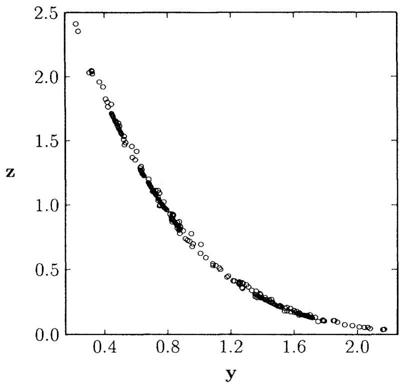

FIG. 2. The Poincaré map constructed from Fig. 1. Open circles, automaton simulation; closed circles, deterministic simulation.

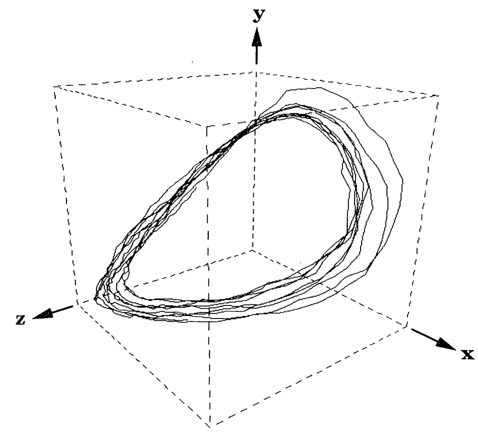

FIG. 3. Noisy limit cycle for the same parameters as Fig. 1 except $\kappa_2 = 1.3$. The box origin is at $(x, y, z) = (0.16056, 0.16938, 1.05147)$ with corners along the x, y, and z axes at 0.55263, 0.85461, and 3.04752, respectively.

the flow with the Poincaré surface of section. The well-defined chaotic bands of the deterministic attractor (cf. Fig. 2) have merged.

The strange attractor arises through a period-doubling cascade and insight into the nature of the internal noise effects on the dynamics can be obtained by considering system parameters in the periodic regime. Figure 3 shows the result of a simulation deep within the period-one regime. Intrinsic noise produces no dramatic effects; it simply produces a "thick" limit cycle in the vicinity of the deterministic limit cycle.

Internal fluctuations have pronounced effects on the dynamics of period one in a parameter range closer to the chaotic regime. Figure 4 shows the Poincaré map of such a noisy attractor. (The attractor itself closely resembles Fig. 1 and is not displayed.) The noisy iterates are again spread out in a linelike fashion with small thickness, reminiscent of the Poincaré map for the chaotic attractor; however, there is concentration of iterates at the Poincaré map fixed point corresponding to the stable limit cycle. Considering the Poincaré map of the flow in the chaotic regime, the strange attractor can be viewed as the closure of the unstable manifold associated with the hyperbolic points of the map [10]. Periodic orbits near the chaotic regime are embedded in this complex hyperbolic manifold structure. Thus, addition of noise to such a system is likely to cause the system to explore the underlying manifold structure and cause the iterates to spread strongly in the unstable directions, just as in the case of the chaotic attractor, except the effect is somewhat more dramatic since one starts with a periodic orbit. These effects have been observed earlier for both external noise [2] and a Langevin model [11]. Figure 4 also shows the Poincaré map for external noise applied to the deterministic rate law. Internal and external noise have a qualitatively similar effect on the phase-space dynamics. This is so in spite of the fact the automaton dynamics does not rely on the existence of a macroscopic rate law, and in a strict sense the deterministic manifold structure that is used to rationalize the behavior of externally forced systems does not exist. The fluctuating automaton dynamics is able to give rise to an incipient or fragmented dynamical structure in the concentration phase space that mimics the unstable manifold structure of the deterministic system and controls the character of the dynamics.

If large system sizes are considered or the reactive collision frequency is increased relative to the nonreactive collision frequency, the unstirred system is unable to maintain its homogeneous character. This leads to desynchronization of local regions in the system and the dynamics takes on a complex spatial as well as temporal character. This is shown in Fig. 5 where the local concentration of

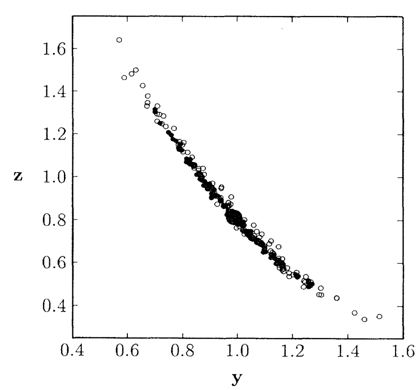

FIG. 4. The Poincaré map for the parameters of Fig. 1 except $\kappa_2 = 1.4$ (open circles). Also shown is the Poincaré map constructed from the rate law (2) with bounded external noise on all three concentrations (closed circles). The noise amplitude was selected to be comparable to that observed in the automaton simulation. The large heavy dot denotes the position of the limit cycle.

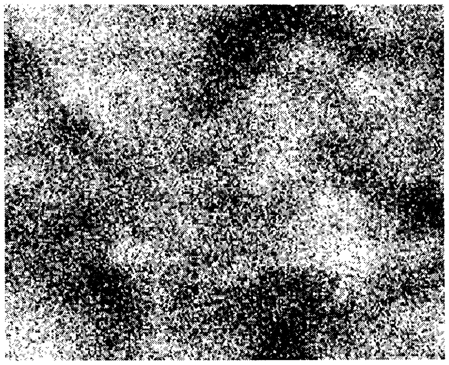

FIG. 5. Simulation for a set of 200×200 lattices with system parameters of Fig. 4 and a diffusion coefficient 10 times smaller. The Z concentration is displayed as gray shades.

the Z chemical species is displayed in the 2D real space. The attractor occupies a smaller volume in phase space due to this desynchronization process. The full investigation of internal noise on such spatiotemporal dynamics is easily carried out in the context of the mesoscopic model described here.

Our calculations have shown that intrinsic fluctuations can have pronounced effects on the dynamics of systems close to and in the chaotic regime. The automaton mean-field equations, which are the mass-action rate equations (2), yield results which differ from the full automaton dynamics due to fluctuations: Deterministic period one is transformed into a noisy "strange attractor" and a strange attractor may suffer dephasing and smoothing. Fluctuations do give rise to significant effects on the scale of the attractor size in phase space [3].

Given these facts it is important to discuss whether the determinisic mass-action rate law is useful for the analysis of the system's dynamics in or near the chaotic regime. One can view the automaton results as experimental observations for a system obeying the automaton microscopic dynamics. If one compares the bifurcation sequence (period-doubling cascade in this case) leading to chaos for the deterministic and automaton dynamics, one observes that internal noise shifts the bifurcation points, limits the number of period doublings that can be observed, and leads to band merging of the deterministic attractor. All of these effects have been noted earlier for external noise applied to nonlinear dynamical systems [2]. Our results show that the deterministic equations along with a knowledge of their manifold structure can be used to predict the general location of the bifurcation sequence in parameter space and the coarse structure of the attractors for the fluctuating medium. The magnitude of the internal fluctuations as a function of the system's parameters can be determined only from the full microscopic dynamics, and quantitative statements regarding attractor modifications cannot be made on the basis of the deterministic equations. With this proviso, one may say that even under finite-amplitude internal noise the macroscopic equations retain some of their predictive power. The observed effects of internal fluctuations are consistent with the structurally stable character of the chaotic flow and the fact that in the chaotic regime the invariant density retains many gross features of its deterministic analog [4].

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