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Has chaos implied by macrovariable equations been justified?

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The underlying microscopic dynamics of a deterministic chemical chaos predicted by phenomenological equations is investigated in this paper. Ensemble simulation of the master equation for the chemical Lorenz model was carried out and compared to the deterministic results. Our calculations reveal that in the chaotic regime the mass action law description is related neither to the ensemble mean nor to the most probable values within the ensemble. The intrinsic fluctuations in this regime also prove to be much more intensive than in other situations. These results propose that the macrovariable equations no longer provide a correct description of the true collective dissipative behavior in the chaotical regime, and a more microscopic description is necessary in this circumstance. [S1063-651X(98)50607-1]

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The investigation of the passage from disordered motion at the molecular level to collective behavior at the macroscopic level has had a long history. At the macroscopic level, the dissipative processes are traditionally described by a set of phenomenological equations. While the microscopic description of disordered molecular motion are physically more fundamental, the macroscopic phenomenological approach is mathematically more convenient. In fact, the theoretical starting point of exploring macroscopic phenomena such as pattern formation or dissipative structures has been frequently a set of deterministic equations [1]. While the investigation at the macroscopic end has proved to be fruitful, it is often desirable to go back to examine the underlying microscopic origins of the macroscopic phenomena. In the present paper, we concentrate our attention on a related specific problem; that is, the microscopic dynamics of deterministic chaos implied by the phenomenological macrovariable equations.

Although low dimensional chaos in dissipative dynamical systems has been widely investigated in nonlinear dynamics, its microscopic origin in the particle reactive and elastic collision and diffusion processes, especially its effect on intrinsic molecular fluctuations, have attracted attention in the past few years [2–9], and have been a topic of considerable controversy [3,4,7]. The interest was aroused by the question whether intrinsic thermodynamical fluctuations, which are always present in real physical systems, can be amplified just as the external disturbance does by the deterministic chaos predicted by the macroscopic equations. Dispute has been focused on the validity of the phenomenological equation descriptions. Previous studies include Fokker-Planck equation analyses and stochastic as well as particle simulations. Specifically, Keizer and Fox analyzed the internal fluctuations by using the master equation formalism as well as simulations with appropriate stochastic differential equations [2]. Their results suggested that deterministic chaotic dynamics can amplify intrinsic fluctuations so that the macrovariable equations are unstable and cannot be contracted from an underlying molecular description. The Brussels group [5–7] conducted comparative studies to investigate the influence of molecular fluctuations through case studies including the spatially distributed Brusselator and the Williamowski-Rössler model. They argued that the deterministic description in the chaotic attractor is robust towards internal noise, and that in a statistical sense the phenomenological equations still keep their significance. The problem has also been studied by lattice gas automaton [8], and quite recently [9] another case study was reported where intrinsic fluctuations were observed to have significantly altered the probablistic structure of the chaotic attractor.

In this Rapid Communication, we examine closely the master equation for the chemical Lorenz model by simulating it in ensembles. Our direct information of the master equation will show that in the chaotic regime, the macroscopic description is no longer useful and cannot be justified from the underlying mesoscopic description.

In the chemical version of the famous Lorenz model [10], the equations are interpreted as derived from the following reaction steps:

$$\begin{array}{ll}
X+Y+Z\xrightarrow{k_1}X+2Z, & A_1+X+Y\xrightarrow{k_2}2X+Y,\\
A_2+X+Y\xrightarrow{k_3}X+2Y, & X+Z\xrightarrow{k_4}X+P_1,\\
Y+Z\xrightarrow{k_5}2Y, & 2X\xrightarrow{k_6}P_2,\\
2Y\xrightarrow{k_7}P_3, & 2Z\xrightarrow{k_8}P_4,\\
A_3+X\xrightarrow{k_9}2X, & X\xrightarrow{k_{10}}P_5,\\
Y\xrightarrow{k_{11}}P_6, & A_4+Y\xrightarrow{k_{12}}2Y,\\
A_5+Z\xrightarrow{k_{13}}2Z, &
\end{array}$$

where k_i $(i=1,2,...,13)$ are rate constants. Concentrations of species A_i $(i,=1,2,...,5)$ and P_i $(i=1,2,...,6)$ are assumed to be constant in order to keep the system out of equilibrium. The mass action kinetics of intermediates in the above reaction network is capable of yielding Lorenz strange attractors with positive values of X,Y,Z under appropriate reaction rate parameters. The chemical Lorenz system thus provides an ideal model of chemical chaos for examining the effect of intrinsic fluctuations on macroscopic chaos.

Within the framework of the birth-death formulation of stochastic theory, the reaction steps are assumed to form a Markov process and the evolution of the system is described by the following master equation:

$$
\begin{aligned}
\frac{\partial}{\partial t} P(X,Y,Z,t) = {} & C_1[X(Y+1)(Z-1)P(X,Y+1,Z-1,t) - XYZP(X,Y,Z,t)] \\
& + C_2[(X-1)YP(X-1,Y,Z,t) - XYP(X,Y,Z,t)] \\
& + C_3[X(Y-1)P(X,Y-1,Z,t) - XYP(X,Y,Z,t)] \\
& + C_4[X(Z+1)P(X,Y,Z+1,t) - XZP(X,Y,Z,t)] \\
& + C_5[(Y-1)(Z+1)P(X,Y-1,Z+1,t) - YZP(X,Y,Z,t)] \\
& + C_6[(X+2)(X+1)P(X+2,Y,Z,t) - X(X-1)P(X,Y,Z,t)] \\
& + C_7[(Y+2)(Y+1)P(X,Y+2,Z,t) - Y(Y-1)P(X,Y,Z,t)] \\
& + C_8[(Z+2)(Z+1)P(X,Y,Z+2,t) - Z(Z-1)P(X,Y,Z,t)] \\
& + C_9[(X-1)P(X-1,Y,Z,t) - XP(X,Y,Z,t)] \\
& + C_{10}[(X+1)P(X+1,Y,Z,t) - XP(X,Y,Z,t)] \\
& + C_{11}[(Y+1)P(X,Y+1,Z,t) - YP(X,Y,Z,t)] \\
& + C_{12}[(Y-1)P(X,Y-1,Z,t) - YP(X,Y,Z,t)] \\
& + C_{13}[(Z-1)P(X,Y,Z-1,t) - ZP(X,Y,Z,t)],
\end{aligned}
\tag{1}
$$

where C_i $(i,1,2,...,13)$ are microscopic reaction constants having incorporated the constant particle numbers of species A_i $(i=1,2,...,5)$. The master equation provides a description of the reaction processes at a more microscopic level and serves as a suitable starting point for examing the microscopic behavior of deterministic chemical chaos. Equation (1) is rather complex and not suitable for analytical solution. An efficient way to solve the chemical master equation is to simulate it directly by applying the standard algorithm originally developed by Gillespie [11]. For our purpose, we carried out a direct stochastic simulation of the Markovian transition processes of the reacting system in an ensemble. The ensemble was created by assigning each run in it same initial particle numbers of species X,Y,Z respectively and different seeds for the random number generator. When the evolution proceeds, quantities of physical significance in the master equation such as the average value, the mean squared deviation, and other various variances can be readily calculated in the ensemble. The most probable values of the species can also be calculated.

We compared the deterministic dynamics of mass action law such as stable fixed points, limit cycles, and chaotic attractors with their counterparts of stochastic simulation. It was found that the phenomenological mass action kinetics can satisfactorily describe the collective behavior of the reaction processes in the neighborhood of stable fixed points and keeps its full validity. Figure 1 shows the ‘‘orbits’’ of the deterministic, the mean, and the most probable values in the vicinity of a stable fixed state. They agree very well with one of the others when approaching uniformly to the common goal. Owing to the limited size of the ensemble, the ‘‘orbit’’ of the most probable value is of zigzag. It should be a smoother curve if the ensemble is sufficiently large. In this case, the internal noise seems to have a trivial effect. When the mass action law predicted a limit cycle, intrinsic noise exhibited considerable influence. The simulated orbit takes on a thick structure and situates in the neighborhood of the well defined deterministic periodic orbit. In the chaotic regime where the mass action law predicts chaotic attractors, the macroscopic description becomes even worse. Figure 2 depicts the sharp contrast of the deterministic chaotic attractor with the mean and the most probable values of simulation. The simulated orbits of the mean and the most probable values are approximately in accordance with each other; however, they do not evolve into a Lorenz strange attractor as implied by the mass action law but tend to approach a small attracting volume in the phase space. The phenomenological equations no longer provide a correct collective description of the underlying chemical Markovian transition processes. They describe neither the mean nor the most probable values of the ensemble. Figure 3 shows the time evolution of the mean squared deviations of simulation for a deterministic fixed point and that for a chaotic attractor is displayed in Fig. 4. These fluctuations grow rapidly, and after a transient period reach final saturation. The initial rapid growth is due to the initial Dirac-δ condition for the prob-

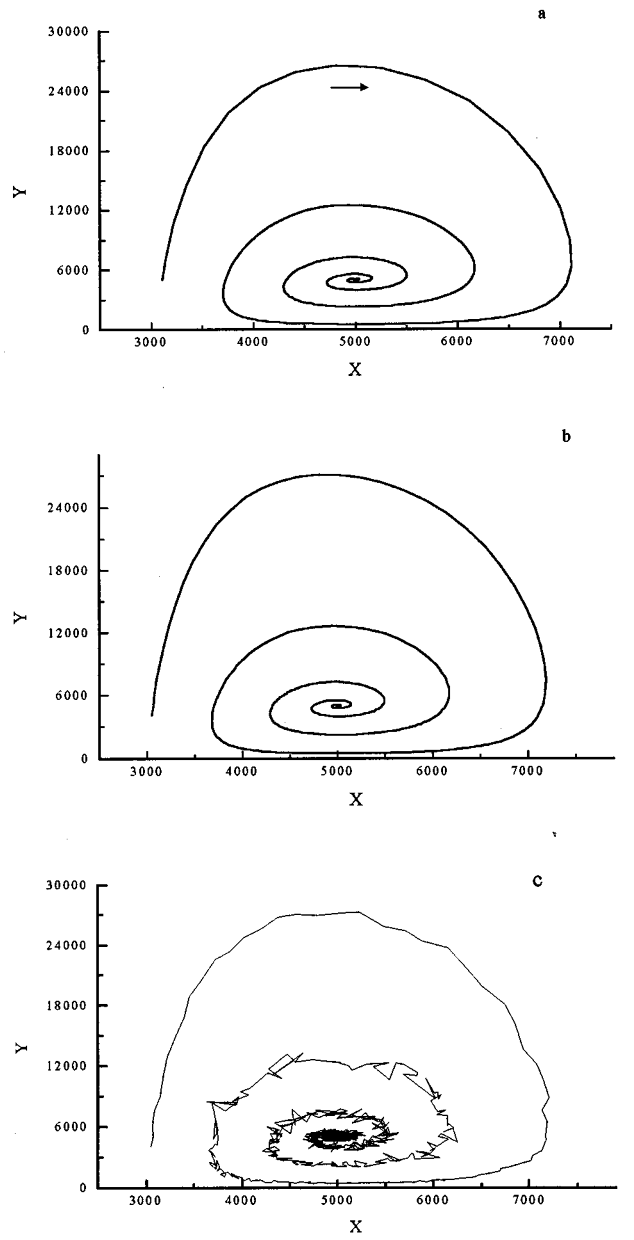

FIG. 1. Comparison between the result of rate law and that of the master equation in the neighborhood of a stable fixed point. The deterministic orbit (a) agrees perfectly well with the mean (b) and the most probable value (c) of stochastic simulation. Reaction parameters are $c_1=0.0004$, $c_2=0.2$, $c_3=0.03$, $c_4=2.0$, $c_5=2.0$, $c_6=0.1$, $c_7=0.01$, $c_8=0.267$, $c_9=1000$, $c_{10}=1000$, $c_{11}=150.0$, $c_{12}=100.0$, $c_{13}=10\,002.67$.

ability $P(X,Y,Z,t)$. The plateau for the deterministic chaos is obviously much higher than that for the fixed stable point. Its intensity is approximately two times that of the fixed point.

Our calculations and comparison of the behavior predicted by the phenomenological description and its mesoscopic analog from the master equation has shown that the deterministic law is no longer useful in predicting the average and the most probable particle number when the deterministic chaos shows up. The fluctuations in the chaotic regime have also proved to be much more intensive than in other situations. These results proposed that the deterministic description is invalid in the chaotic regime. Its significance is fully preserved only in the neighborhood of stable fixed points. Even in the periodic regime, the deterministic prediction is unsatisfactory.

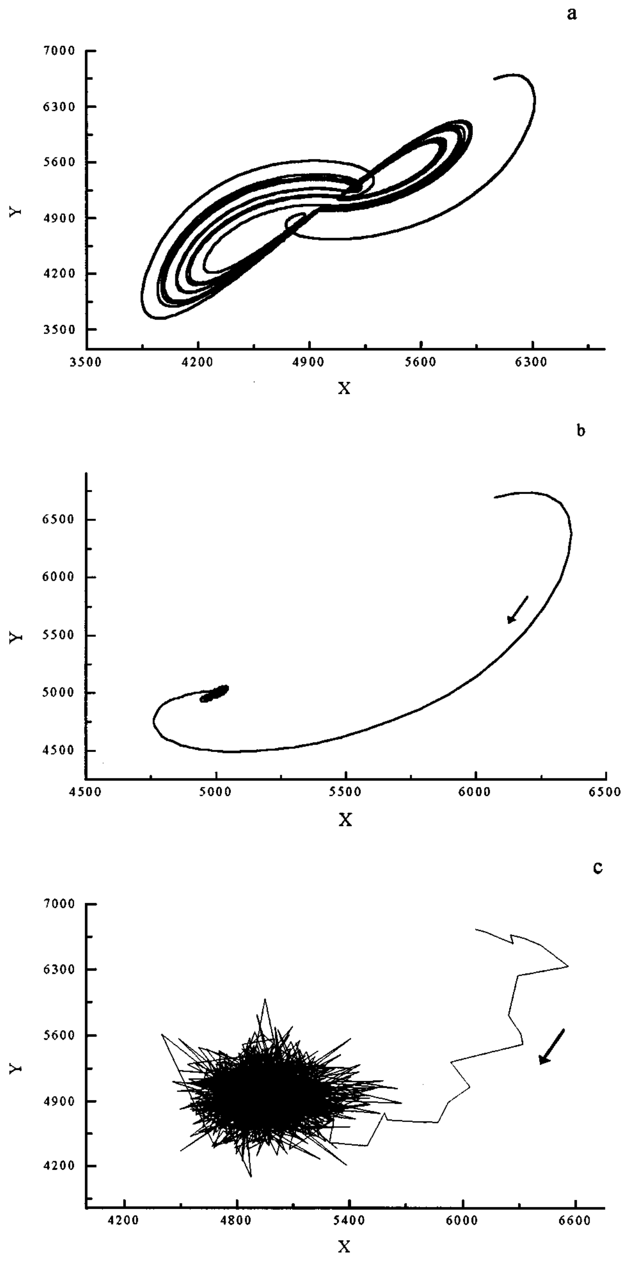

FIG. 2. Phenomenological result and its microscopic analog in the chaotic regime. The deterministic chaotic trajectory (a) predicts neither the mean (b) nor the most probable value (c) of simulation. Parameters are the same with Fig. 1 except that $c_3=0.58$ and $c_{11}=2900.0$.

Compared to previous studies with this problem, our findings are consistent with those reported by Fox and coworkers [2] who used the master equation formalism and simulations with proper stochastic differential equations as well. The results presented here confirm their general conclusion of the invalidity of the phenomenological equations in the regime of deterministic chaos. The effect of molecular

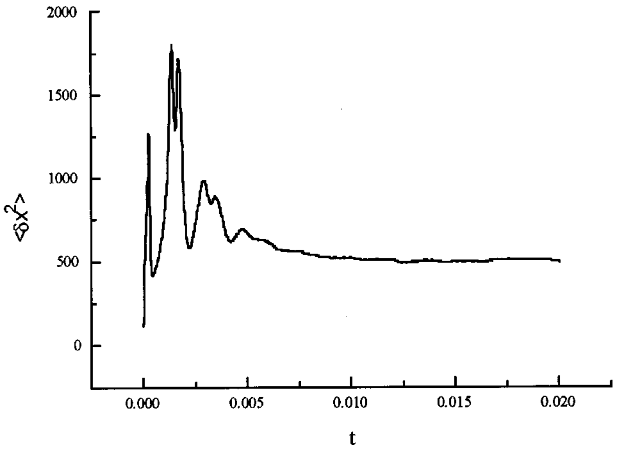

FIG. 3. Time evolution of the mean squared deviation from simulation for X species in the condition where mass action kinetics predicts a stable fixed point. The ensemble consists of 1000 simulation runs.

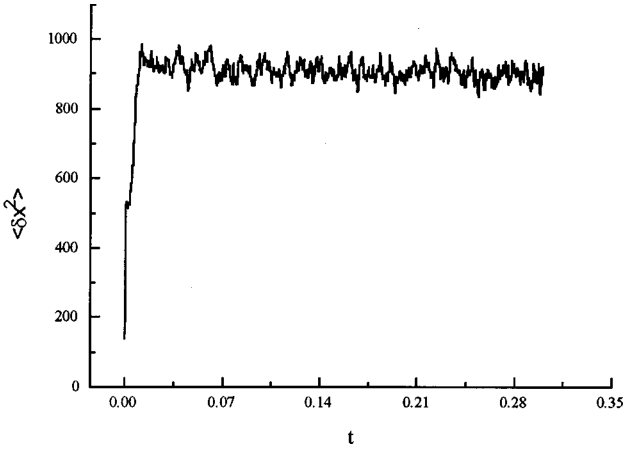

FIG. 4. Time evolution of the mean squared deviation of simulation in the chaotic regime. The fluctuation for X species is approximately two times that in the fixed point regime (see Fig. 3). For calculation of the deviation, 1000 runs were used.

fluctuations on other chemical chaos models have also been previously investigated by stochastic [5,6] as well as reactive lattice gas automaton [8] and particle simulations [7]. However, these researches were limited in the comparison of the properties between an individual chaotic trajectory and a single run of stochastic simulation of the master equation. The more detailed microscopic information in the master equation was ignored. In the Williamowski-Rössler model, chaotic attractors of deterministic law really share some common statistical properties with their analog of a single simulation run. This, however, does not generally apply to other systems. An opposite example is the chemical Lorenz model as reported in Ref. [9]. Our direct simulation of the master equation for the chemical Lorenz model was carried out within a large ensemble, and much more significant properties such as the mean and the most probable value, which is important for evaluating the relevance of the macrovariable equations, were obtained. From our calculations, it can be reasonably concluded that in the chaotic regime the macrovariables and individual chaotic trajectories of the phenomenological description are no longer useful. The macroscopic equations may still keep some relevance in providing some useful information about the bifurcation sequence when the system parameters are varied. When the deterministic chaos shows up, a microscopic or at least mesoscopic description is necessary in order to describe the true behavior of the process.

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