Noise-Induced Bistability in a Monte Carlo Surface-Reaction Model

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(Received 14 February 1989)

We find a noise-induced transition to bistability in a Monte Carlo simulation of a model heterogeneous catalytic chemical reaction which is deterministically monostable. Analysis of the probability density function and the correlation integral of time series of this model indicates the existence and central role of noise in this transition. We find that the behavior of this system is a consequence of the interaction of noise with the spatial degrees of freedom on the model catalytic surface.

PACS numbers: 82.65.Jv, 05.40.+j, 05.45.+b

The interaction of noise with spatial degrees of freedom and its resulting impact on the dynamic behavior of nonlinear systems is a topic of growing interest.[1] Among the ramifications of fluctuations on the dynamic behavior of such systems is the noise-induced transition,[2] which can consist of a transition to bistability in a system that is deterministically monostable in the absence of noise. Noise-induced transitions have been studied with theoretical formulations[3] and observed experimentally in a parametric oscillator[4] and in the T-I–T-II transition in superfluid He II.[5] These studies have emphasized the fact that the effects of noise are often dramatic and nonintuitive. Thus, the understanding of these effects and the systems to which they apply is a significant fundamental problem.

In this Letter, we demonstrate with Monte Carlo simulations the emergence of bistability in the rate of reaction and fractional surface coverage of reactant as a result of fluctuations which stem from the statistical nature of reactant adsorption in a model heterogeneous catalytic chemical reaction. In the classical approach to studying reaction kinetics, analytical models which generally consider spatially averaged concentrations of adsorbed reactant are utilized. The advantage of our modeling approach arises from both the intrinsic microscopic detail and the natural inclusion of spatial inhomogeneity in a Monte Carlo simulation. While deterministic formulations via the classical modeling approach predict monostability in the rate of reaction and surface coverage of this model system, with our approach we find that (i) the catalytic surface in this system is spatially inhomogeneous[6] and (ii) fluctuations in the adsorption of reactant can cause a severe departure from the deterministic description of analytical models. Through manipulation of the rate of reactant desorption in our model, we can control the extent to which fluctuations influence the dynamic behavior of the system and we demonstrate a noise-induced transition from deterministic monostability to bistability in the presence of noise. We also present a novel analysis of the bistable time series of this model utilizing the correlation integral, a measure previously used only in the analysis of deterministic systems.

The model reaction is a generic, bimolecular Langmuir-Hinshelwood reaction:

$$A_g + S \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A\text{-}S\,, \tag{1}$$

$$B_g + S \underset{k_d}{\overset{k_a}{\rightleftharpoons}} B\text{-}S\,, \tag{2}$$

$$A\text{-}S + B\text{-}S \xrightarrow{k_r} AB_g + 2S\,, \tag{3}$$

where A and B are identical, yet distinguishable, gas-phase reactants, S represents a vacant surface site, and k_a, k_d, and k_r are the rate constants for adsorption, desorption, and surface reaction, respectively.

Monte Carlo simulations of this model reaction were conducted on square lattices with periodic boundary conditions. In this Letter, we present the results of simulations run on 32×32 lattices. The size dependence of our results is considered in a separate publication.[7] At the onset of a simulation, the surface is randomly populated with 50% A and 50% B. In the simulation algorithm, a site is selected at random and desorption of the species adsorbed on the site is attempted with a probability of desorption, p_d. If the desorption attempt is unsuccessful, a neighboring site is chosen at random and the two are removed from the surface, simulation reaction, if the pair are an A and a B. One or two reactant adsorptions in which A and B are selected with equal probability immediately succeed each desorption and surface reaction, respectively. In this way, we simulate a system which is reaction limited, a convention chosen for convenience since the kinetic behavior of this model is insensitive to the relative rates of adsorption and reaction.[8] This algorithm is run repeatedly into the long-time regime and the rate of reaction and the fractional surface coverage of A are monitored as a function of time. Time in the simulation is measured in units of Monte Carlo steps (MCS), where one MCS is defined as N desorption or reaction attempts, N being the number of sites on the surface.

Figure 1 shows the rate of reaction as a function of time for several rates of desorption. The rate of reaction is defined as the number of reactions per site per MCS and is measured as an average over 10 MCS. The trend revealed in Fig. 1 is an increase in the noise level of the rate of reaction as p_d is decreased. While fluctuations in

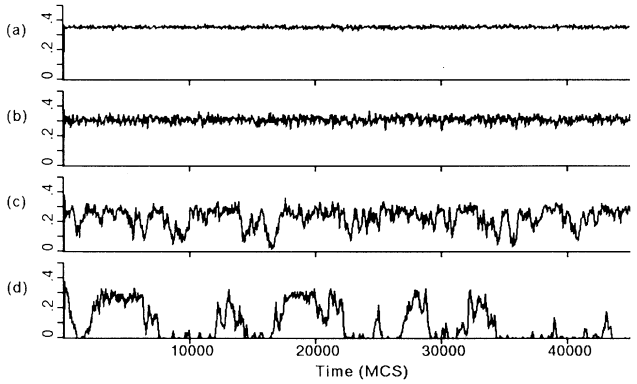

FIG. 1. Rate of reaction (reactions/site MCS) as a function of time (MCS) for (a) $p_d=0.1$, (b) $p_d=0.01$, (c) $p_d=0.001$, and (d) $p_d=0.0001$.

the rate of reaction are quite small at high values of p_d [Figs. 1(a) and 1(b)], they increase to the point of dominating the kinetic behavior of the system at low p_d [Figs. 1(c) and 1(d)].

The transition of our system from monostability to bistability is seen in a plot of the probability density of reactant coverage as a function of p_d. Figure 2, curve *a*, indicates that the distribution of coverage is roughly Gaussian, centered near the mean-field value of $\frac{1}{2}$, at sufficiently high probabilities of desorption. As p_d is decreased, the distribution spreads, as seen in Fig. 2, curve *b*, until it becomes approximately uniform, as shown in curve *c*. As p_d is further decreased, in Fig. 2, curve *d*, the distribution becomes bimodal with peaks at 0 and 1. We observed a similar transition of the rate of reaction probability density, which is Gaussian at high p_d and approximately exponential at low p_d.

The correlation integral provides a quantitative description of the role of noise in the transition of our system from monostability to bistability. We calculated correlation integrals for the time series obtained in our simulations following Grassberger and Procaccia.[9] Figure 3 depicts the results of the analysis of the rate of reaction time series at values of p_d for which the system is monostable [3(a)], in the transition region [3(b)], and bistable [3(c)]. The results obtained with these time series are quantitatively similar to those obtained from analysis of the coverage time series. Figure 3(a), obtained for a Gaussian distribution of coverage, indicates a stationary rate of reaction. The noise level of the system is revealed at small length scales on the plot[10] in which the slopes of the lines are 0.92, 1.92, 2.86, and 3.89 for $d=1$, 2, 3, and 4, respectively. Figure 3(b) indicates that noise has virtually dominated the kinetic behavior of the system for $p_d=0.001$. There is virtually no region of zero slope as noise is present to a much greater extent than in Fig. 3(a). The slopes of the lines on this plot are 0.97 ($d=1$), 1.92 ($d=2$), 2.93 ($d=3$), and 3.88 ($d=4$). At this rate of desorption, the distribution of coverage is approximately uniform. Figure 3(c) was obtained from the bistable time series at $p_d=0.0001$. In this plot, we observe power-law scaling that is independent of the embedding dimension. From the averaged slopes of three such plots at an embedding dimension of 7 ($d=7$), we calculate the correlation exponent to be 0.40 ± 0.03, thus indicating a transition of the system to bistability.

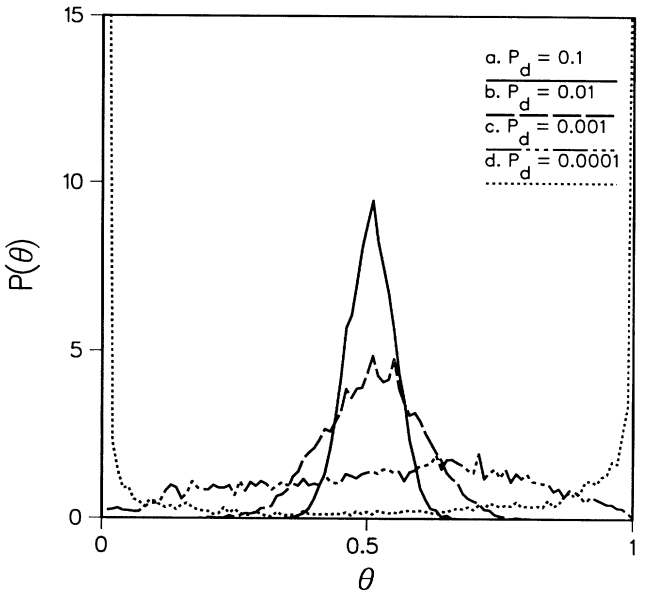

FIG. 2. Probabilty density of the fractional coverage of A for $p_d=0.1$, 0.01, 0.001, and 0.0001. Plots were constructed from time series containing 50000 points each.

The correlation-integral plot is typically utilized to distinguish random time series from time series which stem from deterministic chaos. Our present efforts have shown that this measure can be efficaciously employed in the analysis of time series of systems undergoing noise-induced transitions. However, our results also indicate that caution should be utilized in the interpretation of correlation-integral plots. The fact that these plots have attained a constant slope for time series in the bistable regime of the system does not imply that the oscillatory behavior of this system stems from deterministic chaos. Rather, correlation-integral analysis of this well-defined stochastic system merely indicates the fact that the kinetic behavior of this system is correlated. In this light, we can no longer attach significance to the value of the correlation exponent as the lower bound for the fractal dimension of the strange attractor of the system as, presumably, no such attractor exists in stochastic systems.

Sigeti and Horsthemke[11] have recently shown that stochastic systems can be distinguished from those exhibiting deterministic chaos in the high-frequency limit of the power spectrum. In this formulation, the power spectrum from a system subject to noise should scale as a power law with frequency, ω, as

$$S(\omega)\sim C\omega^{-2n}, \tag{4}$$

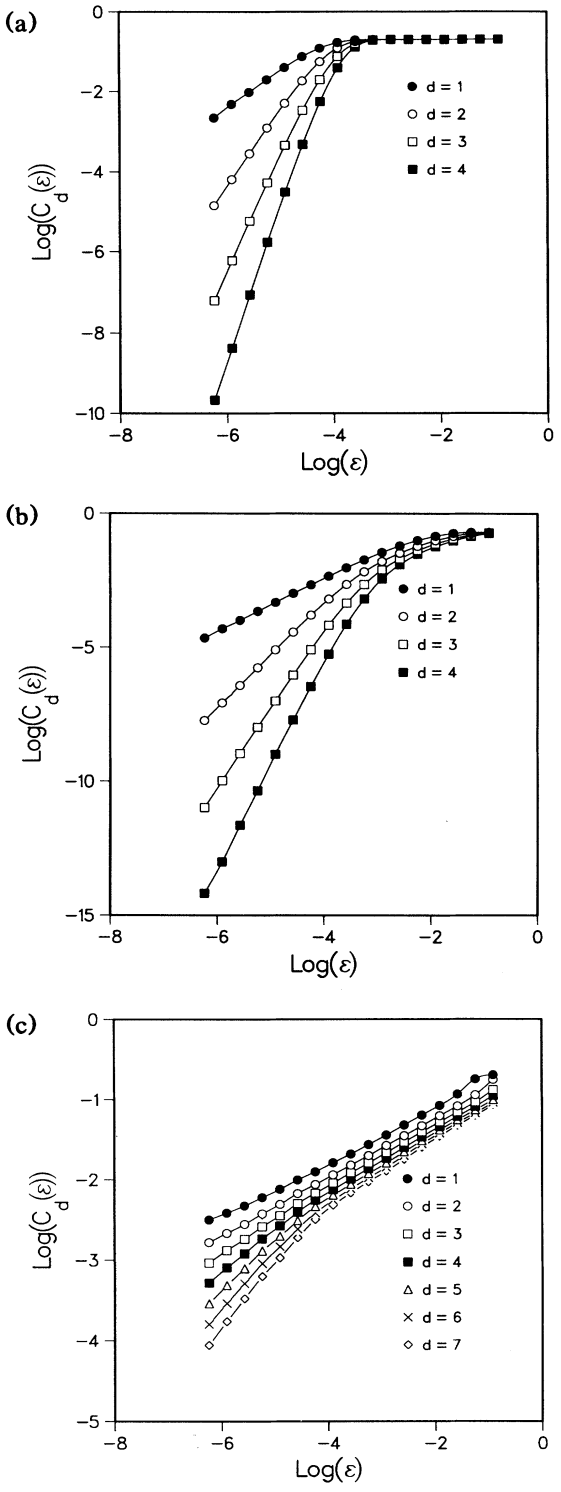

FIG. 3. Log-log plot of the correlation integral, $C_d(\epsilon)$, as a function of ϵ, a length scale in the domain of the time series, for various embedding dimensions, d. All plots were obtained from time series of 10000 points spaced 10 MCS apart. Time series utilized were (a) $p_d = 0.1$, (b) $p_d = 0.001$, and (c) $p_d = 0.0001$.

where n is the number of times the system is removed from white noise (or, equivalently, the sample paths of the process are $n-1$ times differentiable, almost surely). Sigeti and Horsthemke assert that the power spectra of time series resulting from deterministic chaos should scale exponentially with frequency. A representative power spectrum of a bistable time series is depicted in Fig. 4. The scaling of the power spectrum with frequency is of the form of Eq. (4) with $n = -1.005 \pm 0.001$, thus indicating that the oscillations are essentially stochastic. We have confirmed that this scaling results from an exponential autocorrelation function, characteristic of Brownian motion, or internal diffusion of the process from one state to the next. The power spectrum of an exponential autocorrelation function can be easily shown to be

$$S(\omega) = c/(c^2+\omega^2) \tag{5}$$

and, in the high-frequency limit ($\omega^2 \gg c^2$), $S(\omega) \sim \omega^{-2}$. Our results, thus, further confirm the generality of the criterion derived by Sigeti and Horsthemke.

The microscopic detail and the natural inclusion of statistical fluctuations in a Monte Carlo simulation allows significant insight to the observed macroscopic behavior in our system. The erratic behavior of our system represents a dramatic departure from mean-field analysis which would indicate that the loss of A due to bimolecular reaction is exactly offset by its gain due to readsorption, since, in each reaction, a single A is lost and the two resulting vacant sites are replaced by AA, AB, BA, or BB with equal probability. Thus, at steady state, the coverages should retain their initial values of $\frac{1}{2}$ in the absence of fluctuations.

We have discerned that the bistability of this model and departure from the mean-field description arises

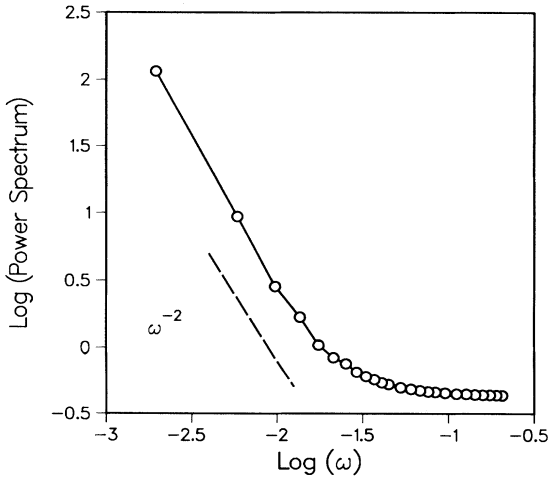

FIG. 4. Log-log plot of the power spectrum of the rate of reaction at $p_d = 0.0001$. The power spectrum is calculated from an average autocorrelation function of the rate-of-reaction time series consisting of 10000 points each.

from fluctuations in the adsorption of reactant that are recorded to an increasing extent on the simulation surface as the probability of desorption is decreased. These fluctuations are reflected on the surface in the form of adsorbate islands which arise as a consequence of the Langmuir-Hinshelwood surface-reaction mechanism. For surface reaction to occur via the Langmuir-Hinshelwood mechanism, species A and B must occupy adjacent sites on the catalytic surface. Adsorbed species surrounded at the nearest-neighbor distance by species of their own type are, thus, excluded from surface reaction and they remain on the surface in the form of islands. For irreversible adsorption ($p_d = 0$), a partitioning of adsorbed species into islands occurs producing a decrease in the rate of reaction with increased segregation of the adsorbed species. This partitioning does not result, however, in a system in which equal amounts of adsorbed species are present; rather, a single species (A or B with equal probability) will always dominate and, eventually, cover the surface completely. This apparent bias arises from statistical fluctuations in the adsorption of reactant.

Reactant adsorption in this model is analogous to the flipping of a fair coin because A and B are chosen to adsorb with equal probability. However, the fact that these species adsorb with equal probability does not mean that equal amounts of A and B adsorb. From considerations which arise from the central limit theorem we know that $2N$ flips of a fair coin do not generally result in N heads and N tails, rather, we expect fluctuations in the outcome of the coin toss to scale as $\sqrt{N}$. In the irreversible limit, the fluctuation in the adsorption of reactant is recorded and grows on the surface because reaction eliminates *exactly equal* amounts of A and B.

For reversible systems (p_d nonzero), the effect of fluctuations is eliminated to an extent determined by the probability of desorption. In systems with sufficiently high desorption probabilities, fluctuations and, thus, island growth are eradicated by desorption, an indiscriminating, first-order process. As the probability of desorption decreases, islands that are dissipative structures form on the simulation surfaces. The growth and subsequent dissipation of these islands creates fluctuations in the rate of reaction. The probability of desorption apparently determines the average size to which these islands will grow and, thus, the extent of noise present in the rate of reaction. As p_d is decreased, a critical value is eventually reached for which islands grow to the dimension of the lattice. The transition to bistability in our system occurs at this threshold of irreversibility.

It should be noted that the above arguments imply a size dependence of the behavior of this model. Thus, a noise-induced transition occurring from statistical gas-phase fluctuations is limited to small surfaces. However, we expect our observations with statistical fluctuations to hold on larger surfaces in environments with gas-phase fluctuations of a nonstatistical nature due to imperfect mixing of the gas phase, for example. Apparently, the factor governing noise-induced bistability in surface-reaction systems is the relative magnitude of the fluctuations to the size of the surface.

In summary, we have demonstrated the occurrence of a noise-induced transition from monostability to bistability in a simplified model of a heterogeneous catalytic chemical reaction. The probability density of coverage and correlation-integral analysis indicate the existence and the central role of noise in this transition. Also, analysis of the power spectrum of time series in the bistable regime confirms that the behavior of this system is influenced by noise. The Monte Carlo approach to modeling the reaction kinetics in this system has allowed the elucidation of the transition because of the spatial degrees of freedom and noise inherent in this computational technique and, thus, demonstrates the utility of Monte Carlo simulations in the study of nonlinear systems.

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