Scaling structure and $1/f$ noise in one-dimensional surface-reaction models

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We study a one-dimensional $A + B \rightarrow AB$ catalytic surface reaction model. The simulation and analysis by using the master equation and its approximate form (Fokker-Planck equation) both show that the system exhibits scaling structure and $1/f$ noise when the rate of desorption p_d is equal to $1/(N+1)$, where N is the number of sites on the surface. In addition, based upon this model, another one-dimensional $A + B \rightarrow AB$ reaction model which exhibits self-organized criticality and $1/f$ noise behavior is also constructed.

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The scientific interest in the dynamic behavior of the catalytic reaction systems has grown during the past years [1]. Especially, the oxidation of carbon monoxide on platinum is extensively studied. One of the important features is the self-oscillations in the rate of reaction which has been found experimentally in these catalytic systems. There have been varieties of theoretical ways to study the kinetics of catalytic reaction, among these, the Monte Carlo method, utilized by Fichthorn and his coworkers recently [2–5], is demonstrated to be a feasible way. In Refs. [4] and [5], they proposed a very simple two-dimensional reaction model, i.e., the $A + B \rightarrow AB$ model. In that model the reaction mechanism is the Langnuir-Hinshelwood reaction. With low rates of desorption of the species (A and B), this model can explain the self-sustained oscillations of the reaction rate and the fractional coverage of A or B on the catalytic surface. Besides, through computer simulations, they found that the oscillations observed are a finite-size effect. In this paper, we study the the one-dimensional version of the reaction model. Our study is mainly limited to the one-dimensional system for three reasons. First, the one-dimensional model already displays a very rich behavior. Second, with modern computer facilities numerical simulations of sufficiently high quality are possible in the one-dimensional system. Third, this model is realistic for the actual reaction on a ringlike catalytic system. We will concentrate our attention on the rate of reaction, because it determines the amount of the radiation energy and can be measured experimentally. We analyze this model by using the master equation and its approximate form (Fokker-Planck equation). (This analysis is also effective for the two-dimensional reaction model in Ref. [5].) The analysis shows that the kinetic behavior of the system is related with not only the rate of desorption but also the size of the system. Moreover, the rate of desorption and the size dependence of the kinetic behavior is drawn quantitatively. At the critical state the system exhibits scaling structure and $1/f$ noise. The Monte Carlo simulation on this model also leads to the same results. Based upon this analysis, another reaction model that exhibits self-organized criticality and $1/f$ noise behavior is also constructed.

The model mechanism is the Langmuir-Hinshelwood reaction

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

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

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

where A and B are reactants and the subscript g denotes the gas phase, S represents a vacant surface site, k_a, k_d, and k_r are the rate constants for adsorption, desorption, and surface reaction, respectively. The model reaction is conducted on a one-dimensional lattice with a periodic boundary condition that represents the catalytic surface. At the beginning of the reaction, the surface is randomly populated with 50% A and 50% B. Then a site is selected randomly and desorption of the species adsorbed on the site is attempted with a probability of desorption, p_d. If the desorption is successful, the reactant on this site is replaced by another reactant, which is chosen among A and B with the same probability. If the desorption is unsuccessful, another site among the two neighboring sites is also chosen at random, and if the pair is an A and a B, reaction takes place and the two are removed from the surface. Succeeding the reaction, two reactants among A and B are immediately chosen with the same probability to adsorb to the two reaction sites.

Now let us analyze this model by using the method of the master equation. Assuming that the surface is in the

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state x at time t, in which the number of A is x while the number of B is $N-x$. Here N is the total number of sites on the surface lattice and is assumed to be considerably large. If a site of the surface is selected randomly at this time, A and B will be chosen with a probability x/N, $1-x/N$, respectively. The transition rate from state x to state $(x+1)$ is denoted by $G(x,t)$ and that to state $(x-1)$ denoted by $R(x,t)$. When the desorption rate of species on the surface is p_d, we may get

$$G(x,t) = \frac{p_d}{2}\left(1-\frac{x}{N}\right) + \frac{1-p_d}{2}\frac{x}{N}\left(1-\frac{x}{N}\right), \quad (4a)$$

$$R(x,t) = \frac{p_d}{2}\frac{x}{N} + \frac{1-p_d}{2}\frac{x}{N}\left(1-\frac{x}{N}\right). \quad (4b)$$

From Eqs. (4a) and (4b), we can see that G and R both do not contain t explicitly and only depend on the intensive quantity θ, here $\theta = x/N$ is the fractional coverage of A. Hence we have

$$G(x) = \tilde{G}(\theta) = \frac{p_d}{2}(1-\theta) + \frac{1-p_d}{2}\theta(1-\theta), \quad (5a)$$

$$R(x) = \tilde{R}(\theta) = \frac{p_d}{2}\theta + \frac{1-p_d}{2}\theta(1-\theta). \quad (5b)$$

The equation of evolution for the probability density $W(x,t)$ of surface state x is given by the well-known master equation

$$\frac{\partial W(x,t)}{\partial t} = G(x-1)W(x-1,t) - G(x)W(x,t) + R(x+1)W(x+1,t) - R(x)W(x,t), \quad \text{for } x = 0,\ 1,\ldots,N, \quad (6)$$

with $W(-1,t) = W(N+1,t) = 0$. This equation is a statistical description of the evolution process, and it is exact in the large N limit. In the special case $p_d = 0$, taking $\frac{\partial W(\theta,t)}{\partial t} = 0$ in Eq. (6), one can obtain immediately the stationary state. It is

$$W(x) \propto \delta_{x,0} + \delta_{x,N}, \quad (7a)$$

or, expressed in θ which, for large N, may be considered approximately as a continuous variable varying between 0 and 1,

$$W(\theta) = \delta(\theta) + \delta(1-\theta), \quad (7b)$$

which has two isolated peaks at $\theta = 0$ and $\theta = 1$, respectively. It means that the catalytic surface is completely occupied by either A or B.

If $p_d \neq 0$, it is not easy to find the stationary state by direct inspection. Fortunately, the probability density $W(x,t)$ is no longer a singular function, we may write the master equation (6) in the form of the Kramers-Moyal expansion

$$\frac{\partial W(x,t)}{\partial t} = \sum_{i=1}^{n}(\partial/\partial x)D^{(n)}(x)W(x,t), \quad (8a)$$

where the Kramers-Moyal coefficents are given by

$$D^{(n)}(x) = (1/n!)[G(x) + (-1)^n R(x)]. \quad (8b)$$

Note that the rates $\tilde{G}$ and $\tilde{R}$ depend only on the intensive quantity θ. Equations (8a) and (8b) can be expressed as

$$\frac{\partial W(\theta,t)}{\partial t} = \sum_{i=1}^{n}(\partial/\partial\theta)D^{(n)}(\theta)W(\theta,t), \quad (9a)$$

where the Kramers-Moyal coefficents are given by

$$D^{(n)}(\theta) = \frac{1}{n!N^n}[\tilde{G}(\theta) + (-1)^n\tilde{R}(\theta)]. \quad (9b)$$

When the size N of the system is considerably large, we truncate expansion (9a) after the second term and obtain the following Fokker-Planck equation [6]:

$$\frac{\partial W(\theta,t)}{\partial t} = \left[-\frac{\partial}{\partial\theta}D^{(1)}(\theta) + \frac{\partial^2}{\partial\theta^2}D^{(2)}(\theta)\right]W(\theta,t), \quad (10a)$$

where $D^{(1)}(\theta)$ and $D^{(2)}(\theta)$ are drift and diffusion coefficients and read

$$D^{(1)}(\theta) = \frac{1}{N}[\tilde{G}(\theta) - \tilde{R}(\theta)] = \frac{1}{N}\left(\frac{p_d}{2} - p_d\theta\right), \quad (10b)$$

$$D^{(2)}(\theta) = \frac{1}{2!N^2}[\tilde{G}(\theta) + \tilde{R}(\theta)] = \frac{1}{2N^2}\left[\frac{p_d}{2} + (1-p_d)\theta(1-\theta)\right]. \quad (10c)$$

For the stationary state $\frac{\partial W(\theta,t)}{\partial t} = 0$, we can get easily the solutions $W(\theta)$ of Eq. (10a) with (10b) and (10c)

$$W(\theta) \propto \frac{1}{D^{(2)}(\theta)}\exp\left[\int^{\theta}\frac{D^{(1)}(\theta')}{D^{(2)}(\theta')}\,d\theta'\right]. \quad (11)$$

First, in the case of $p_d = 1$, the probability density has the form

$$W(\theta) \propto \exp\{2N\theta(1-\theta)\}, \quad (12)$$

which is a Gaussian distribution, centered at $\theta = 1/2$. Second, when $p_d = p_{d0} \equiv \frac{1}{N+1}$, the probability density $W(\theta)$ of the the fractional coverage θ of A is independent of θ, i.e.,

$$W(\theta) = \text{const}, \quad (13)$$

which we mark as the critical state. Obviously, when $p_{d0} < p_d \leq 1$, the distribution of coverage has only one peak at $\theta = 1/2$, which corresponds to a monostable mode. When $0 < p_d < p_{d0}$, the distribution of coverage is bimodal with peaks at $\theta = 0$ and $\theta = 1$.

When the rate of desorption p_d decreased from 1 to p_{d0} to 0, the surface state undergoes a transition from monostable states to bistable states. When $p_d = p_{d0} = \frac{1}{N+1}$, the surface is at the critical state with the distribution of coverage of A or B being constant. Obviously, the fluctuations in the coverage scale are of the order of the square root of the number of sites on the surface when $p_d = 1$ and there do not exist fluctuations in the coverage when $p_d = 0$. However, when $p_d = p_{d0}$, the fluctuations

in the coverage can be calculated through Eq. (13), i.e., $\Delta\theta^2 = \langle\theta^2\rangle - \langle\theta\rangle^2 = \frac{1}{12}$, which is independent of the size of system, where the symbol $\langle\ \rangle$ represents the average of the corresponding quantity bracketed. According to the definition of the rate of reaction in Ref. 5, the fluctuations in the rate of reaction are in agreement with the fluctuations in the coverage. Therefore, in general, by decreasing the rate of desorption, the kinetic behavior ranges from steady to oscillatory and then to virtually poisoning, and the surface undergoes a transition from deterministic monostability to bistability. These results are in accordance with the results obtained in Refs. [4] and [5]. Monte Carlo simulations on this one-dimensional reaction model also show that the p_d dependence of the distribution of coverage, fluctuations in the rate of reaction, and the fractional coverage of A or B are the same as those given in Refs. [4] and [5] (see Figs. 1 and 2 in Ref. [4]).

In addition, the kinetic behavior of the catalytic system is closely related to its size. In fact, for a given value of p_d, by changing the size of the catalytic surface (hence the value of p_{d0}), we can let the system satisfy $p_d > p_{d0}$ or $p_d = p_{d0}$ or $p_d < p_{d0}$, i.e., we can make the system undergo a transition from a monostable state to a critical state or to a bistable state and *vice versa*. Corresponding to such transitions, the fluctuations in the rate of reaction and the coverage may enhance or weaken or even disappear. The change of the system size can be realized by dividing the surface or by covering the surface with alumina paint and removing the cover from the surface, as in Ref. [7].

Simulations were also run in order to examine the scaling property and the power spectrum of the rate of reaction when the system is in the critical state. The rates of desorption are always chosen to be $p_d = p_{d0} = \frac{1}{N+1}$ in the simulation. After a certain transient time, the system enters the critical state which is independent of the initial configuration. First, the distribution functions $D(s)$ of clusters for different sizes of lattice N are calculated, where s is the cluster size (a cluster contains only A or only B). We find that $D(s)$ obeys the following scaling law

$$D(s) \propto s^{-\beta} \tag{14}$$

with s varying in a wide range. Here β is a constant. Taking the finite-size effect into account, we try to fit these functions by a multifractal form

$$\frac{\log_{10} D(s)}{\log_{10}(N/N_0)} = g_s\left(\frac{\log_{10}(s/s_0)}{\log_{10}(N/N_0)}\right). \tag{15}$$

Here $g_s(x)$ is a scaling function. With $s_0 = 1.5$ and $1/N_0 = 4.5$, these distribution functions can be fitted very well, which indicates that lattices with different sizes N belong to the same universality. The result is shown in Fig. 1. This result shows that the system is scale invariant with respect to cluster sizes. It is a character of fractal. Second, the rate of reaction is recorded as a function of time. Time in our simulation is also measured in units of Monte Carlo steps (MCS) which are defined as the time for N desorption or reaction attempts. The rate of reaction is defined as the number of reactions per site per MCS and is measured as an average over 2 MCS. Figure 2 shows the fluctuations in the rate of reaction with $N = 4000$. There is a self-similar structure in the curve. Figure 3 shows the power spectrum of the rate of reaction. The result is obtained by squaring the Fourier transformation of the rate of reaction, and the curve in Fig. 3 has been smoothed by averaging over 0.05 unit of $\log_{10} f$. From this figure, one sees that the power spectrum has the form of $1/f^{\alpha}$ with $\alpha = 1.1 \pm 0.1$ over a wide range. One can also see that the larger the size of the lattice, the wider the range is, which indicates that the $1/f$ noise obtained here is not a finite-size effect. A power spectrum with this form indicates that the oscillations are correlated, which is different from that in the bistable state case where the power spectrum has the form of $1/f^2$ and, therefore, the oscillations are essentially stochastic [4]. In fact, the existence of the correlation of oscillations in different time is just the reason why the phase transition between the monostable state and the bistable state may occur.

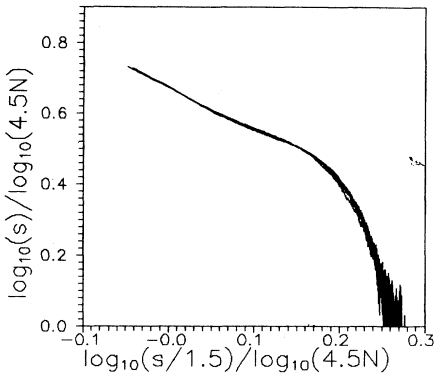

FIG. 1. Multifractal scaling plot of the distribution functions $D(s)$ of the cluster size s in the critical state. The sizes of the system are 1000, 2000, 3000, 4000, and 5000, respectively.

Based upon the above analysis, we construct another

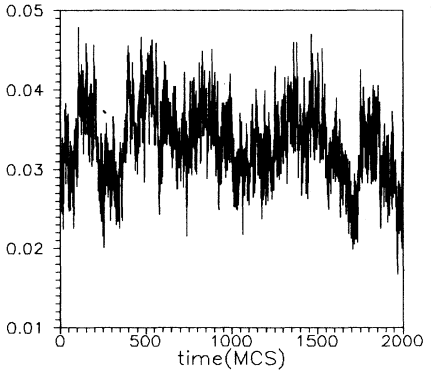

FIG. 2. The rate of reaction as a function of time (MCS) in the critical state. Here $N = 4000$ and $p_d = \frac{1}{4000+1}$ and only 2000 data are given.

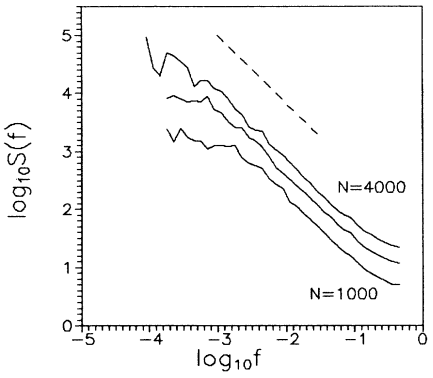

FIG. 3. The power spectra of the rates of reaction in the critical state. The sizes of the system are 1000, 2000, and 4000, respectively. The dashed line shows the form of $1/f^{1.1}$.

slightly different reaction model $A + B \rightarrow AB$. The only difference from the above model is that the rate of desorption of every site on the surface is assumed to be negligible, meanwhile the system is driven by "slow noise"—random local perturbations every MCS, which makes the species absorbed on one site of the surface desorb. Here one MCS is defined as N reaction attempts. The noise introduced here is similar with that in the theoretical sandpile models [8–11] where a particle is added until the preceding avalanche has terminated. Obviously, this new model can approximately satisfy the condition $p_d = p_{d0} = \frac{1}{N+1}$ as in the above model statistically. Moreover, due to the large size of the system, the system can keep in or near the critical state if the frequency of disturbance to the system has little change. So this model can reach the critical state naturally. Simulations on this improved model show that the distribution function $D(s)$ also satisfy the scaling law (14), the distribution functions $D(s)$ of different sizes of systems can be fitted together very well by using the multifractal form, and the power spectrum of the rate of reaction exhibits the behavior of $1/f^{\alpha}$ with $\alpha = 1.1 + 0.1$ over a wide range. Because the scaling property and the power spectra of the rates of reaction for this model are very similar to those of the above model, the plots of $D(s)$ and the power spectra of the rates of reaction are left out. In Ref. 8, the concept of self-organized criticality was introduced, and was expected to be a bridge between fractal and $1/f$ noise. The feature of the system is scale invariant when it is in the critical state reached through a self-organized process without the fine tuning of any parameter. Therefore, the present model can be considered as one of the models that exhibits self-organization criticality with both scale invariance and $1/f$ noise.

In conclusion, we have studied a one-dimensional catalytic surface reaction model, that exhibits scaling structure and $1/f$ noise when the rate of desorption p_d is equal to its critical value. We have also proposed an improved model that exhibits self-organized criticality. For this improved model, the system can spontaneously reach the critical state, in which the system is scale invariant and the power spectrum of the rate of reaction has the form of $1/f$. If accompanying the reaction there is something radiating, then the radiation also exhibits the behavior of the $1/f$ noise, and it might be regarded as an explanation about the light from quasars [12].

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