Dynamic behavior of the Ziff-Gulari-Barshad model on fractal lattices: The influence of the order of ramification

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(Received 5 April 1999)

A catalytic reaction model, the Ziff-Gulari-Barshad model, is studied on fractal lattices, and the influence of the order of ramification of the lattice on the dynamic behavior of the model is investigated. According to the Monte Carlo simulation results, the order of ramification of the lattice is not crucial to the existence of the continuous transition. This is different from the equilibrium phase transitions in discrete-symmetry spin models (such as the Ising model). Our results indicate that the criterion of the existence of the reactive phase may be complicated. [S1063-651X(99)11609-X]

PACS number(s): 05.50.+q, 82.65.Jv, 64.60.Ht, 61.43.Hv

I. INTRODUCTION

In recent years, nonequilibrium phase transitions, occurring in surface reaction models, have attracted great interest. In 1986, Ziff, Gulari, and Barshad (ZGB) proposed a simple nonequilibrium model to account for a chemical reaction process of the catalytic oxidation of CO on the Pt surface [1]. The ZGB model assumes a Langmuir-Hinshelwood mechanism, i.e.,

$$\mathrm{CO}+*\rightarrow \mathrm{CO}^* \quad \text{with probability } p, \tag{1a}$$

$$\mathrm{O_2}+2*\rightarrow 2\mathrm{O}^* \quad \text{with probability} 1-p, \tag{1b}$$

$$\mathrm{O}^*+\mathrm{CO}^*\rightarrow \mathrm{CO_2}\uparrow+2* \quad \text{for nearest neighbors}, \tag{1c}$$

where $*$ denotes an empty site of the surface, and O* and CO* denote the adsorbed O atom and CO molecule, respectively. The mole fraction of CO in the gas phase, p, is the only parameter in the model.

The ZGB model is too simple to thoroughly describe the actual catalytic process [2,3]. However, it shows rich interesting phenomena in physics. On the two-dimensional lattices, the ZGB model shows three phases [1,4]; when p is lower than p_1, the system is finally saturated by O; if p is greater than p_2, the surface is eventually fully covered by CO; and if $p_1<p<p_2$, the system falls into a reactive phase. The transition at p_1 is continuous, while at p_2 it is first order. It has been shown that the continuous transition at p_1 belongs to the directed percolation (DP) or Reggeon field theory class [5,6]. The first order transition at p_2 has been studied by the constant Θ method [7].

Since the pioneer work of ZGB [1], other surface reaction models have been introduced to investigate the nonequilibrium phase transitions, e.g., the monomer-monomer models [8–15], dimer-dimer models [16–19], and monomer-dimer-monomer models [20].

However, the real catalytic surfaces are not purely two-dimensional and translationally invariant since they may contain defects and may be poisoned by a foreign and inert species. Therefore, it is important to investigate the influence of the geometrical structure of the reactive substrate on the kinetics and the nonequilibrium transitions. In order to do so, it is convenient to treat the catalytic surfaces as fractal lattices. Recently, the monomer-monomer model on fractal lattices, such as the percolation clusters, has been studied both theoretically and numerically [21]. It was found that the structural changes on the lattice strongly affect the reactivity of the catalysis. The monomer-dimer models have also been studied on the percolation clusters [22,23] and the Sierpinski type fractals [24,25] by the Monte Carlo simulations, and the influence of the fractal dimension of the lattice on critical points were discussed.

It is well known that the physical properties on the fractal lattices are very different from those on translationally invariant lattices. There are several geometric parameters to describe a fractal. In our previous work [26], the influence of the lacunarity of the lattice on the dynamic scaling behavior of the ZGB model was studied, and the critical exponents δ, η, and z at the continuous transition are calculated for different lattices. We found that the continuous transitions of the ZGB model on fractal lattices with different lacunarities belong to different universality classes even if the lattices have the same fractal dimension.

Besides the lacunarity L, the order of ramification R is another important parameter to describe a fractal. The order of ramification R at a point P is equal to the number of significant bonds, which one must cut in order to isolate an arbitrarily large bounded set of points connected to P (see [27–30]). In the problems of equilibrium phase transitions in discrete-symmetry spin models (such as the Ising model), the order of ramification plays an important role. It has been considered that, on the fractal lattices with finite order of ramification, the short-range discrete-symmetry spin models show no finite-temperature phase transitions while, on the lattices with infinite order of ramification, these models undergo a phase transition at $T_c>0$ [29–31].

In this paper we study the ZGB model on fractal lattices and investigate the influence of the order of ramification of the lattice on the nonequilibrium transitions. Several fractal lattices with finite order of ramification are employed to

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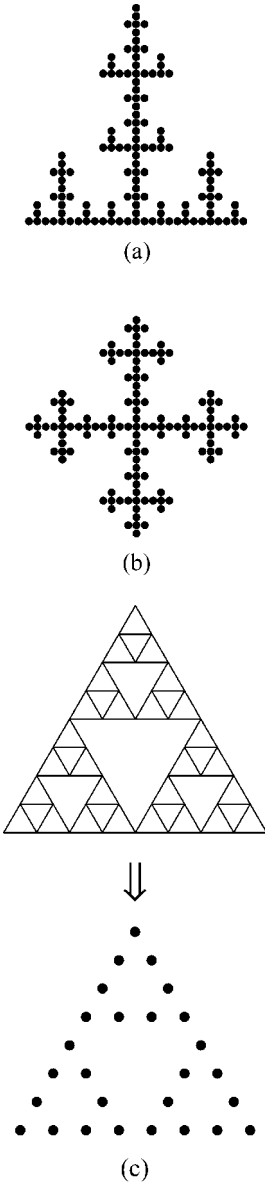

FIG. 1. Third stage of the three lattices: (a) $\mathcal{L}_1$ lattice, (b) $\mathcal{L}_2$ lattice, and (c) $\mathcal{L}_3$ lattice.

serve as the catalytic surface. It is found that on some of the lattices the ZGB model does not show the reactive phase, i.e., the continuous transition does not exist, while on the other lattices the reactive phase exists. This suggests that the order of the ramification of the lattice is not crucial on determining the existence of the continuous transition in the ZGB model. This is very different from the problems of equilibrium phase transitions in discrete-symmetry spin models. Tretyakov and Takayasu have considered that the critical dimension for the monomer-dimer catalysis model is probably 1. However, our results indicate that the criterion of the existence of the reactive phase may be complicated.

II. SIMULATIONS

Here we study the ZGB model on three kinds of fractal lattices, viz. $\mathcal{L}_1$, $\mathcal{L}_2$, and $\mathcal{L}_3$, which are shown in Fig. 1. $\mathcal{L}_1$ and $\mathcal{L}_2$ are treelike lattices (with no loops), while $\mathcal{L}_3$ is a Sierpinski-gasket-type lattice (with loops). Each of the three

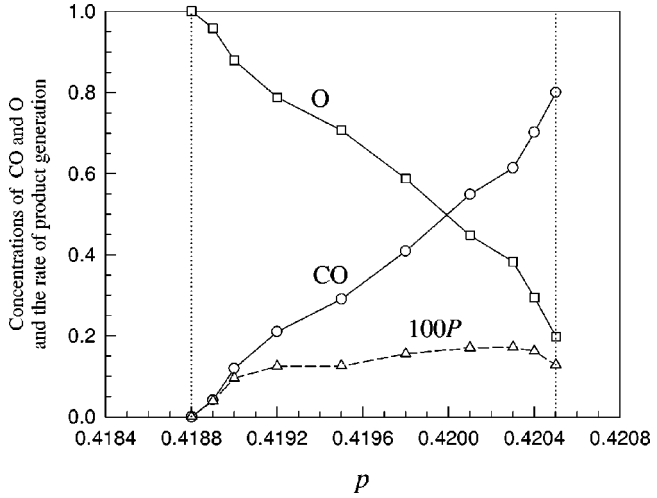

FIG. 2. Phase diagram of the ZGB model on the lattice $\mathcal{L}_1$, where the curves marked CO and O are the concentrations of CO and O on the catalytic surface, respectively, and P is the rate of the product generation (the curve shown in this figure is 100 times the rate).

lattices has a finite order of ramification ($R<\infty$).

The lattices $\mathcal{L}_1$ and $\mathcal{L}_2$ are constructed as follows. Consider a square of unit area and subdivide it into $3^2=9$ subsquares, among which $2^2=4$ subsquares are cut out. Then one gets the first stage of the structure. The lattice sites are located in the center of the subsquares. For $\mathcal{L}_1$ and $\mathcal{L}_2$, the eliminated subsquares are differently selected [see Figs. 1(a) and 1(b)]. Both of them have no loops. The fractal dimension of the two lattices is $d_f^{(\mathcal{L}_1)}=d_f^{(\mathcal{L}_2)}=\ln(9-4)/\ln 3\simeq 1.465$. The linear dimension of lattices $\mathcal{L}_1$ and $\mathcal{L}_2$ in our simulations is taken to be $3^6=729$ (the total number of sites on the lattices is 15 625). In order to check the system size dependence, several simulations on the seventh construction stage of the fractal lattices (with a linear dimension of $3^7=2187$) are run, and no significant differences are detected.

The lattice $\mathcal{L}_3$ is a Sierpinski-gasket-type fractal. One starts with a triangle and then connects the midpoints of the edges, creating four small triangles, among which three are upward and the central one is downward. The central small triangle is then removed and one gets the first construction stage of a Sierpinski gasket. The procedure is repeated for the three upward small triangles. The lattice sites of $\mathcal{L}_3$ are located at the center of each smallest upward triangle [see Fig. 1(c)], so $\mathcal{L}_3$ is the dual lattice of the Sierpinski gasket, and it has loops. In our simulations we use the ninth construction stage of this lattice (the total number of sites is 59 049). The same results are also obtained for the tenth construction stage.

The simulations start with an empty lattice. During the simulations, a list of vacant sites is maintained. A monomer (CO) or dimer (O_2) is randomly selected to deposit into the lattice. If it is a monomer, a vacant lattice site is chosen at random, and the monomer is added to the site. Then the time is increased by $1/N_v$, where N_v is the number of the empty sites. If the selected species is the dimer, a vacant site is randomly chosen. Then one of its nearest-neighbor sites is checked. If the nearest-neighbor site is also empty, the dimer is adsorbed onto the two sites and dissociates immediately.

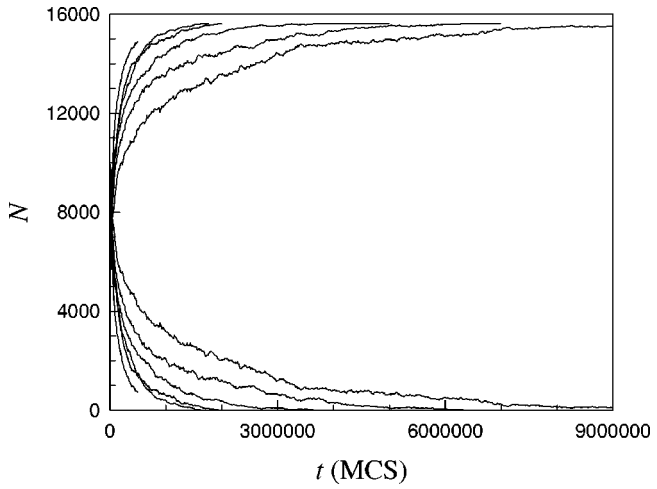

FIG. 3. Dependence of the number of lattice sites (N) occupied by CO (the upper curves) and CO (the lower curves) on time for the lattice $\mathcal{L}_1$ for different values of p ($p>p_c$). From left to right, $p=0.4211$, 0.4210, 0.4209, 0.4208, 0.4207, and 0.4206. The total number of the lattice sites is 15 625. The unit of time is a Monte Carlo step.

In both cases, the time is increased by $1/N_v$. If the adsorbed CO molecule (O atom) is the nearest neighbor of an O atom (a CO molecule), they react and desorb from the lattice immediately.

For $\mathcal{L}_1$, the phase diagram is shown in Fig. 2 from which one can see that there are three phases and two transition points $p_1 \approx 0.4188$ and $p_2 \approx 0.4205$. In the case $p<p_1$ ($p>p_2$), the system is finally saturated with O (CO). Between the two points is the reactive region, in which the system falls into a steady state. In Fig. 2, the rate of the product generation, P, which is defined as the mean number of product species (CO_2) generated for each attempted deposition of CO and O_2, is also shown. From the figure, one can see that both the reactive region and the rate of product generation are very small. The numbers of lattice sites occupied by O and CO vs time are shown in Fig. 3 for some values of $p>p_2$. The same data are replotted as a function of $(p-0.420\,53)t$, which are shown in Fig. 4, and a reasonable

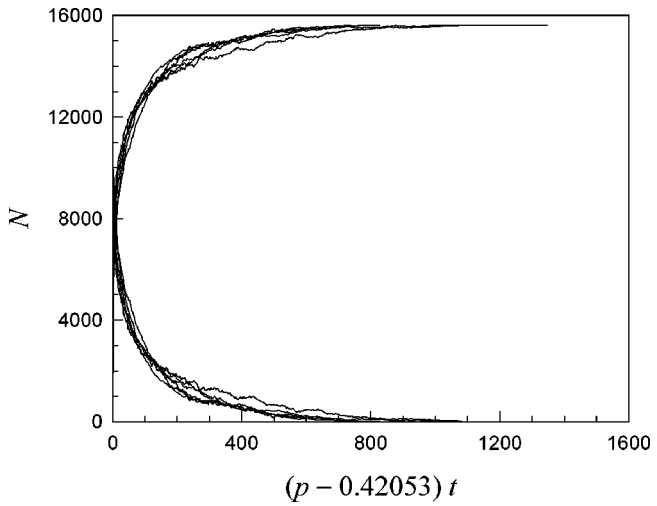

FIG. 4. Same data of Fig. 3 as a function of $(p-0.420\,53)t$. This crude scaling procedure indicates $p_2 \approx 0.420\,53$.

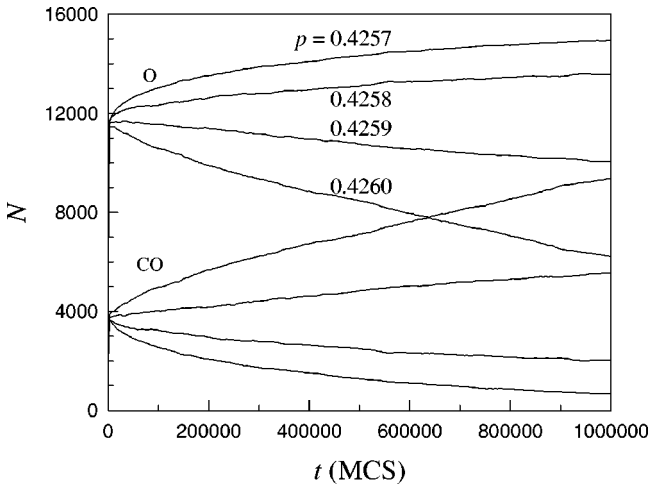

FIG. 5. Dependency of the number of lattice sites occupied by O and CO on time for the lattice $\mathcal{L}_2$ for different p. The total number of the lattice sites is 15 625.

good data collapse is found which gives an estimate for p_2 ($p_2 \approx 0.420\,53$) [4]. Taken together, these results indicate that $p_2 = 0.4205 \pm 0.0001$.

For $\mathcal{L}_2$ and $\mathcal{L}_3$, the numbers of lattice sites occupied by O and CO vs time are shown in Figs. 5 and 6, respectively, for different values of p. From the figures one can see that, for either $\mathcal{L}_2$ or $\mathcal{L}_3$, there is only one critical point p_c. When $p<p_c$, the system is finally saturated with O, and if $p>p_c$, the lattice is ultimately fully covered by CO. For $\mathcal{L}_2$, $p_c = 0.4258 \pm 0.0002$, while for $\mathcal{L}_3$, $p_c \simeq 0.4493 \pm 0.0002$. These results suggest that the ZGB model on $\mathcal{L}_2$ and $\mathcal{L}_3$ shows no reactive phase, i.e., there is no range of p values over which a steady state with nonzero O and CO site concentrations exists. This behavior is quite similar to that in the one-dimensional case [4].

III. REMARKS

In 1992, Ziff and Brosilow suggested a method, viz. the constant Θ method, to investigate the first order transition of

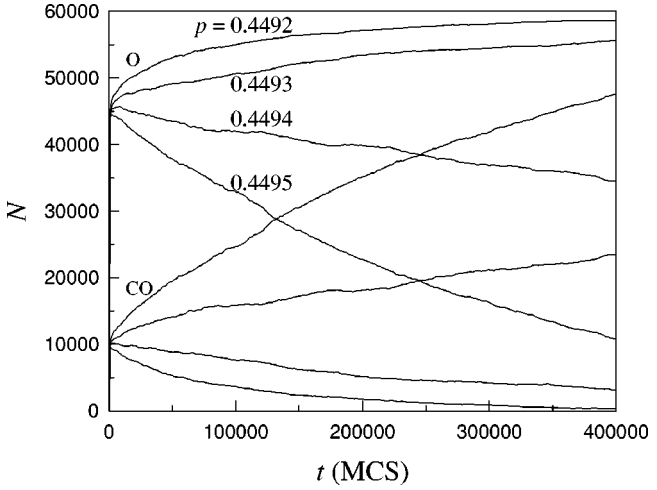

FIG. 6. Dependency of the number of lattice sites occupied by O and CO on time for the lattice $\mathcal{L}_3$ for different p. The total number of the lattice sites is 59 049.

the ZGB model on a square lattice [7]. The main idea is, when simulating the catalytic reaction process, to try to fix the concentration of adsorbed CO to a given value Θ. When it is lower than Θ, let a CO molecule deposit to the lattice, otherwise, an O_2 molecule is considered. Of course, one can also try to fix the concentration of adsorbed O to a given value. Ziff and Brosilow discussed that this ''constant Θ process'' is equivalent to the ''constant *p* process.'' The constant Θ method gives the good estimation of the first order transition point [7]. However, this method does not always work for fractal lattices, especially for the ones with finite order of ramification. On these lattices, there are only a few paths to connect two lattice sites, which makes the same species concentrate and form large clusters more easily. Therefore, the reactive regions between the clusters become very small, so the local adsorption events are time relevant but not random.

The ZGB model on the one-dimensional lattice has been studied by Meakin and Scalapino [4], and they found that the reactive phase does not appear in this case. In 1991, Tretyakov and Takayasu studied the ZGB model on a Sierpinski gasket [24] and found that the reactive phase appears. According these results, they have considered that the critical dimension for the ZGB model is probably 1.

Both the one-dimensional lattice studied by Meakin and Scalapino [4], and the Sierpinski gasket studied by Tretyakov and Takayasu [24], are with a finite order of ramification. In the present work, the dynamic behavior of the ZGB model is studied on another three kinds of fractal lattices with finite orders of ramification. It is found that for the lattice $\mathcal{L}_1$ there exists a reactive phase, and for $\mathcal{L}_2$ and $\mathcal{L}_3$ there is no such phase. All of these results indicate that the order of the ramification of the lattice is not crucial to determine the existence of the continuous transition in the ZGB model, and the criterion of the existence of the reactive phase may be complicated.

ACKNOWLEDGMENTS

This work was supported by the National Basic Research Project ''Nonlinear Science'' and the National Natural Science Foundation of China under Grant No. 19775008.

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